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A STUDY OF HAZARDOUS WASTE MATERIALS, HAZARDOUS EFFECTS AND DISPOSAL METHODS

VOLUME II

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Volume II of this three-volume inventory of hazardous wastes in the United States covers Standard Industrial Classification numbers 10, 11, 12, 20, 22, 26, 28, 282, 283, 284, 285, 287, and 2892. Among the information given for these industries are the source and production, industrial consumption, future outlook, waste characteristics, associated hazards, economic statistics, waste disposal processes and practices, industry description, and major raw materials.

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*Standard industrial classifications, Metal mining, Textile mill products, Chemicals and allied products, Perfumes, Cosmetics, Toilet preparations

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Volume II

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Booz Allen Applied Research, Inc.
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The Solid Waste Research Laboratory of the National Environmental Research Center, Cincinnati, U.S. Environmental Protection Agency, has reviewed this report and approved its publication. Approval does not signify that the contents necessarily reflect the views and policies of this laboratory or of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

The study reported here in three volumes was designed to present background information on hazardous materials for the report to Congress on "National Disposal Study Sites." All persons involved in disposing of or concerned with hazardous wastes will find these volumes of interest.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

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APPENDIX A-1

SIC 10—METAL MINING

1. INTRODUCTION

Mining as discussed in this section includes the extraction of naturally occurring, such as solid minerals including coal. Liquids, such as crude petroleum and natural gas, are treated elsewhere in this report. The activities of quarrying, milling (crushing, screening, washing, flotation, etc.), and other preparation needed to render the material marketable are also included.

It is estimated that, to date, mineral industry solid wastes have accumulated to a staggering 23 billion tons, and have covered over 1.8 million acres. Those wastes heaped into manmade mountains or impounded behind acres of tailing dams, create serious environmental degradation and land use problems primarily in areas experiencing urban and industrial growth. In addition air and water pollution resulting from denuded waste banks and settling ponds, and the emission of noxious and even toxic gases and smoke from burning coal banks, have contributed significantly to the degeneration of the environment.

This section will discuss the mining industry with primary emphasis being placed on the degree of environmental degradation contributed by this industry (SIC 10). The discussion is presented in two parts, as follows:

- Mine Industryal Wastes—This section deals generally with the mining associated wastes, since the type wastes and the methods in which they are produced are similar. Mining's contributions to solid, water, and air pollution are discussed.
- Individual Minerals—This section discusses the individual minerals and includes a brief description of the mineral and its source, production, and industrial consumption pattern, future outlook, waste characteristics, and associated hazards.

The information in this section was mainly obtained from References 1, 2, and 3.

(1) Mine Industry Wastes

1. Solid Waste

The industrial processes involving the mining, milling, smelting and refining of minerals produce solid wastes at each step. The bulk of this solid wastes consists of discarded material from open pit mines, mills, coal preparation plants, blast furnaces, smelters, and refineries or processing plants. Many of these waste accumulations contain millions of dollars worth of unrecovered mineral values, and as such present a challenge to our technology.

Surface mining has disturbed an estimated 3.2 million acres (5,000 square miles) in this country. In 1966 along, strip mining displaced 3.3 billion tons of overburden. Much of the overburden and unacceptable ore was redeposited in mined-out areas, but more than 300 million tons were dumped on adjacent lands for construction of mill tailings, ponds, or leading dumps. The remainder was heaped in piles. Approximately 95 percent of the acreage disrupted by surface mining involved seven commodites: (1) coal, 41 percent; (2) sand and gravel, 26 percent; (3) stone, gold, clay, phosphate, and iron together, about 28 percent; and (4) all others, 5 percent (Reference 4).

Underground mining wastes are attributed to 6,500 active mines and an estimated 90,000 abandoned mines in the United States. About 76 percent are coal mines, 21 percent are metal mines, and 3 percent are nonmetallic mineral mines. In 1966 subsurface mining accounted for 66 percent of domestic coal production, 17 percent of the metal ore tonnage, and 6 percent of the nonmetallic ore tonnage.

At the present annual rate of mineral production, strip mining will disrupt 153,000 acres to yield 3.0 billion tons of crude ores, while underground production will provide an additional 508 million tons of ore. The solid wastes derived from these activities will accumulate at a rate of 3.4 billion tons per year by 1985.

The results of this waste accumulation are seen in the denudation of land, water pollution, alteration of surface and subsurface drainage patterns, clogging of stream channels, fish kills, flooding, air pollution, waste bank fires, land use conflicts, and general disruption to the total ecological balance. An estimated dollar figure for reclaiming the mineral industries solid waste is set in excess of $757 million.

Tables A-1-1 and A-1-2 present sources and magnitudes of solid wastes generated by the minerals and fossil fuel industries up to and including 1968. Table A-1-3 shows the classification methods in terms of physiographic effects of their resultant solid wastes.

Table A-1-1
Solid Wastes Generated by the Mineral and Fossil Fuel Mining and Processing Industries in 1968 and Accumulated up to 1968
(1,000 Short Tons)

Industry	1968	Accumulated up to 1968
Copper	669,683	9,078,544
Iron and Steel	310,764	4,687,858
Phosphate Rock	411,700	1,945,144
Lead-Zinc	22,246	492,525
Alumina	7,976	61,521
Bituminous Coal	97,107	1,849,145
Anthracite Coal	------	910,000
Coal Ash	29,735	455,773
Other	234,538	4,576,281
Total	1,783,749	24,055,791

Table A-1-2

Solid Wastes by Type Generated by the Minerals and Fossil Fuel Industries in 1968

(1,000 Short Tons)

Industry	Mine Waste*	Mill Tailings	Washing Plant Rejects	Slag	Processing Plant Wastes	Total
Copper	492,634	172,751	-------	4,298	-------	669,683
Iron and Steel	157,518	135,798	-------	16,133	1,315	310,764
Phosphate Rock	282,184	-------	110,078	4,543	14,895	411,700
Lead-Zinc	3,504	18,577	-------	165	-------	22,246
Alumina	2,340	682	-------	-------	4,954	7,976
Coal:						
Bituminous	-------	-------	97,107	-------	-------	97,107
Anthracite	-------	-------	-------	-------	-------	-------
Coal Ash	-------	-------	-------	-------	29,735	29,735
Other	144,003	90,535	NA	NA	NA	234,538
TOTAL	1,082,183	418,343	207,185	25,139	50,899	1,783,749

*Includes overburden moved during surface mining activities and waste removed from underground mines, excludes overburden displaced by surface coal mining operations.

NA = Not Available.

Table A-1-3
Mining Classification in Terms of Physiographic Effects

Mining Method Categories	Metals (d)		Fuels (Primarily Coal)		Industrial Minerals (d)	
	Examples Metal Mining	Tailings and Waste	Examples Coal Mining	Spoil and Waste	Examples Industrial Minerals	Spoil and Waste
Open Cast Primarily long term operations exceeding periods of 40 years; some extending to 100 or more years. Includes many quarries.	Most western porphyry copper deposits in Arizona, Utah, Nevada, etc. Also iron mining in Lake Superior region and west.	Usually extensive with copper, less with iron. No serious pollution problem as a rule	Relatively few really long term operations although coal stripping has persisted regionally since about 1910 in Pa., West Va., and Ohio.	Extensive overburden, shale, slate, and some culm Scarring of landscape.	Primarily quarring of granite, trap rock, limestone, marble, etc. Exists throughout the nation. Some quarries over 150 years old.	Usually some waste but not a serious problem. Pits are extensive. Pollution not serious.
Strip Mining Primarily short term operations, some of which are possibly only a year in duration but most of them less than 40 years maximum.	Smaller copper and iron pits, a few base metal operations and occasionally gold. Some uranium mining.	Similar to above but on smaller scale.	Extensive in Pa., West Va., Ky., Ohio, Indiana, Illinois, and some in Wyoming, Iowa, Kansas, Missouri, Utah, Montana, etc.	Extensive and can become a pollution problem. Extensive scarring of area mined.	Borax mining in Mohave region and phosphate rock in Western States. Also gravel pits, sand pits, and clay pits.	Scarring of terrain. Some waste and pollution may occur on small scale.
Caving An underground method of mining that may be long or short term, but leaves glory holes or area of ground subsidence.	Molybdenum mining in Colo. Zinc mining in N.J., some iron in Lake Superior region and Pa.	Tailings vary but can be extensive as for moly mining in Colo.	Not too common today although there was past caving in Pa. Some in Washington.	Large pits left but tailings or waste less extensive.	Occasional caving operations such as Riverside, Cal. or Coshocton, Ohio, for cement materials.	Some waste but no serious problems. Large pits left.
Stope and Underground (Misc.) (c) There are numerous methods of stoping which may or may not influence surface physiography except where back filling becomes involved.	Base and precious metal mining in general: Cour d'Alene, Leadville, Homestake, Butte, Tri-State, Tennessee and tungsten mining.	Tailings and waste rock extensive but less fines than in category No. 1	Room and piller mining largely and various forms of stoping in Pa., Illinois, West Va., Ohio. Anthracite mining in N.W. Pa. Largely historical.	Cob and culm waste extensive plus ground subsidence.	Potash mining in New Mexico and some clays in Mo. and elsewhere. talc and gypsum in N.Y.	Not too serious.
Hydraulic Mining Involves the use of monitor nozzles or water flow. Usually not a long term method and depends upon an available water supply and consisting of material being mined.	Not too much being done today. Was extensive some years ago in Alaska for gold. Some in Colo., S.D., and Idaho in past.	Tailings generally sluiced down stream. Problems largely historical.	Not important,	Scars left by water cuts.	None of importance	— — — — —
Dredging (a) Largely historical in U.S. although there are exceptions. Requires water and may be done on small as well as large scale. Usually short term operations less than 40 years.	Primarily California and Alaska. Extensive in California and Colorado before 1900 for gold. Some in Idaho and Nevada for precious metals. Tungsten and	Coarse spoil piles a problem on Yuba River and some at Leadville, Fairplay etc. Colorado	Some in Ohio and other eastern rivers. Never too extensive.	Largely sediments returned to river.	Often combined operations, Florida phosphates are largest. Combined operations using dredge and drag line techniques. Western phosphates.	Well controlled and not serious.
Special Cases (b) Oil shale mining, Colorado primarily. Some Ilmenite operations, such as in N. J. and certain types of operations difficult to classify. Liguite might be included. Augur or high wall mirung would probably be included here but could be placed in category No. 2. Frasch sulfur operations in Gulf States would also be in this classification	Reclaiming of tailings and slag heaps.	Usually still have tailings problems.	High wall mining in Ky. and West Va. (category No. 2) Liguite in Minnesota and N.D.	Same as category No. 2	Oil shale not extensive. Ilmenite and rulite largely involve beach sands.	Not currently serious problem.

Footnotes

(a) Would include some drag line operations for precious metals
(b) Solution mining or wells not included.
(c) Can be further broken down based on roof support.
(d) For exact statistics, see Table 8 of U.S.B.M. Yearbook (Technologic Trends, etc.) 1962. Classifies surface and underground.

2. Water Wastes

Water is basic to man's existence. Presently, there is a sufficient quantity available for the foreseeable future; however, quality is a factor. More than 90 percent of the earth's water is salty, and the remainder fresh. Due to the accumulative nature of pollutants, only a small percentage of this fresh water is suitable for municipal, agricultural, and industrial use without first undergoing costly treatment. Today, nearly every major fresh water course or lake suffers to some extent from the cumulative effects of pollution.

At present about 1 percent of the estimated 99,000 billion gallons of water used domestically is used by the mineral industry. However, pollution resulting from decades of mining and mineral processing has produced adverse environmental conditions. Industry associated pollution can be separated into three categories: (1) physical pollution, (2) chemical pollution, and (3) combination of both.

- Physical Pollutants—Solid particulate material, either mineral or organic, which enters a stream or pond. These particulates may chemically react with water or other substances to form even more harmful compounds. An estimated total of 2,000 abandoned mine and mill waste dumps are contributing to water pollution. Stabilization of these ponds by planting vegetation is hindered by the high acidity or alkalinity of the material. Studies indicate that sediment yields from strip mines is 1,000 times that derived from forested areas, and that half of the 4.2 million gallons of waste processing water is released untreated to adjacent streams. This sediment may also include valuable mineral resources.

- Chemcial Pollutants—Acids, alkaline solutions, mineral salts draining from mines, and waste heaps accrued from the mining and processing mineral sulfide ores. This type of pollutant is more difficult to treat than solids.

The mineral sulfides react chemically with air and water to form sulfuric acid, which reacts with water and other minerals to cause other ions, such as aluminum, manganese, lead, zinc, and arsenic, to be added to water. These could get into water by draining from spoil material or ground water percolation through spoil material on its way to nearby streams. When the concentration of these pollutants is sufficiently great, "dead water" which is toxic to living organisms results. Table A-1-4 compares unpolluted surface water to some polluted waters of the Eastern Coal Fields.

Table A-1-4
Comparison of Unpolluted Surface Waters with Polluted Waters of the Eastern Coal Fields

Parameter	Unpolluted Waters Mg/liter	Polluted Coal Field Water	
		Moderately Polluted Mg/liter	Heavily Polluted Mg/liter
Sulfide ---------	0 - 20	21 - 249	250+
Total iron ------	0 - 0.3	0.4 - 0.9	1.0+
Manganese -------	0 - 0.05	0.06 - 0.9	1.0+
Aluminum --------	0 -	0.1 - 0.4	0.5+
Hardness --------	0 - 150	151 - 249	250+
Dissolved Solids	0 - 250	251 - 499	500+
Suspended Solids	0 - 100	101 - 249	250+
pH* -------------	6 - 9	5 - 6	2 - 5

*A pH is neutral on a scale of 14, values higher than 7 indicate alkalinity and values less than 7 indicate acidity.

Another effect of acid drainage from these wastes is the formation called "yellow boy," a rust-colored precipitate of ferric hydroxide that accumulates in stream beds. Due to its coating action it smothers aquatic life (coats gill structures), and seals stream bottoms to the extent that water can no longer percolate through the bed to oxygenate and therefore breeding areas for aquatic species are reduced.

Physical and Chemical Pollutants—Compounds such as heavy media and flotation reagents used in cleaning, milling, and beneficiation processes for the recovery of mineral values are inadvertently lost, and reach streams by spills, direct flushing, or from overflows of natural leaching of tailing ponds. Normally, they will be impounded in the settling areas, but seepage through, or breaks in, the dam permit these compounds to contaminate ground waters and streams. Most of these effluents are foul smelling and discolor the water, and in some instances they are toxic. Phosphates in water are believed to stimulate abnormal growth of algae and other aquatic flora, whose demand for oxygen is responsible for the suffication of many forms of stream life.

Physical and chemical pollutants from all types of mining has adversely affected 18,000 miles of streams in the United States. These sources contribute large volumes of sediment, more than 4 million tons of sulfuric acid, to the stream. Surface mining alone has adversely affected 8,700 miles of streams. Underground mining is responsible for degrading approximately 9,300 miles of stream and 22,000 acres of lakes and other water bodies in 31 states (Table A-1-5).

Table A-1-5
Fish and Wildlife Habitat Adversely Affected by Strip and Surface Mining in the United States
(As of January 1, 1967)*

State	Streams		Natural lakes		Reservoirs and impoundments		Wildlife habitat
	Miles	Surface acres	Number	Surface acres	Number	Surface acres	Acres
Alabama	275	1,700	......	......	7	16,300	12,000
Alaska	60	500	......	......	......	......	1,000
Arizona	30	200	......	......	......	......	30,000
Arkansas	150	700	2	200	......	......	32,400
California	320	834	3	70	1	4	61,270
Colorado	880	1,930	......	......	13	600	21,515
Connecticut	62	415	2	100	......	......	16,783
Delaware	(2)	(2)	......	......	5	200	6,000
Florida	(2)	(2)	......	......	......	......	41,000
Georgia	185	510	......	......	10	390	800
Hawaii	......	......	......	......	......	......	355
Idaho	134	654	......	......	......	......	16,460
Illinois	60	350	......	......	50	500	132,395
Indiana	90	750	......	......	......	......	108,744
Iowa	......	......	......	......	......	......	......
Kansas	100	614	......	......	2	50	38,500
Kentucky	395	7,000	......	......	......	......	66,700
Louisiana	1,714	42,500	250	100,000	......	......	3,000
Maine	4	5	......	......	......	......	33,274
Maryland	115	500	......	......	1	72	7,500
Massachusetts	6	600	......	......	......	......	50
Michigan	253	506	16	1,560	32	900	30,729
Minnesota	......	......	6	1,600	......	......	**
Mississippi	30	190	......	......	1	300	1,900
Missouri	330	2,550	......	......	2	6,000	29,500
Montana	136	234	......	......	......	......	10,830
Nebraska	700	21,600	......	......	......	......	16,915
Nevada	41	31	......	......	......	......	**
New Hampshire	35	1,500	......	......	......	......	1,000
New Jersey	10	90	......	......	......	......	**
New Mexico	100	1,150	......	......	1	2	47,540
New York	24	100	2	100	......	......	26,350
North Carolina	......	......	......	......	......	......	850
North Dakota	......	......	......	......	......	......	33,140
Ohio	1,200	1,200	......	......	1	120	67,920
Oklahoma	20	73	......	......	......	......	28,386
Oregon	310	620	......	......	......	......	13,666
Pennsylvania	3,000	9,100	......	......	4	2,020	392,000
Rhode Island	2	1	......	......	......	......	310
South Carolina	......	......	......	......	......	......	800
South Dakota	640	3,250	......	......	33	9,275	23,000
Tennessee	350	3,983	......	......	1	100	20,000
Texas	......	......	......	......	......	......	146,087
Utah	16	90	......	......	......	......	11,434
Vermont	32	70	......	......	......	......	**
Virginia	260	1,015	......	......	......	......	6,000
Washington	64	640	......	......	......	......	......
West Virginia	755	28,015	......	......	4	4,683	149,185
Wisconsin	**	**	**	**	**	**	......
Wyoming	10	200	......	......	......	......	NA
Total	12,898	135,970	281	103,630	168	41,516	1,687,288

NA – Not Available

* Compiled from data obtained from state fish and game personnel.

** Insignificant.

3. Air Wastes

The adverse environmental effects of air pollution that may be attributed to the production, processing, use, and disposal of minerals and fossil fuels amount to about 86 percent of the total problem. Table A-1-6 describes the deleterious effects of mineral-industry-related air pollution. The two principal categories are:

- Dust—Generated during practically every mining and processing operation, dust poses a fourfold menace: (1) creates uncomfortable working conditions; (2) reduces operational life of equipment; (3) creates unhealthy working and living conditions; (4) effects are spread beyond mine or mill site. The principal cause of dust pollution is neglect, e. g. failure to return fine spoils to mined-out areas, or failure to seal the surfaces of waste banks or settling ponds with chemical soil binders, or poor site selection for waste by not considering wind conditions, topography, and proximity of roads or communities.

- Gases— This pollutant results primarily from the use of fossil fuels and the preparation of various mineral commodities through smelting. Sulfur dioxide is emitted by all sources, which in the presence of sunlight and other mineral salts, combines with water to produce sulfuric acid. This combines with other particulates to produce smog. During smelting of the various metal ores, the sulfides are driven off as sulfur dioxide that can be recovered as sulfuric acid or liquid sulfur dioxide. Table A-1-7 lists the type of ore and amount of sulfur oxide recovered (Reference 5).

Table A-1-6
Deleterious Effects of Mineral-Industry-Related Air Pollution

Nature of Pollutants	Causes	Deleterious Effects
Dust	1. Blasting, loading, and hauling of mine run ore	1. -8. Airborne dust which: Darkens the sky Impairs visibility Creates hazardous driving and flying conditions Coats buildings, vegetation, machinery, mine and mill structures Discolors all it falls on Shortens the operational life of equipment Causes respiratory diseases Creates uncomfortable and unhealthy working and living conditions Smothers and/or poisons vegetation and those who feed upon it Degrades land and aesthetic values Pollutes bodies of water upon which it falls
	2. Crushing of ore preparatory to processing	
	3. Drying up of settling ponds and tailing dams	
	4. Overly acid, alkaline, or sterile nature of fine wastes	
	5. Poor waste bank site selection in relation to prevailing winds	
	6. Failure to return fine wastes to mined out areas	
	7. Failure to use chemical soil stabilizers when wastes will not support vegetation	
	8. Failure to cover fine wastes with coarse material or top soil	
	9. Saltation transport of sand size waste material	9. Inundation of surrounding lands, blockage of nearby drainages and roads
	10. Burning of fossil fuels and combustible solid wastes	10. Emission of smoke and other particulate matter

Table A-1-6
(Continued)

Nature of Pollutants	Causes	Deleterious Effects
Gases	1. Combustion of fossil fuels and other burnable solid wastes 2. Slacking of spoils and oxidation of pyritic and carbonaceous wastes 3. Smelting of mine run ores	1.-3. Emission of noxious and toxic gases: Sulfur dioxide Hydrogen sulfide Carbon monoxide Carbon dioxide Hydrocarbons Nitrogen oxides Fluorides Chlorine Ammonia These emissions combine in photochemical reactions to produce smog, sulfuric acid, and nitric acid mists In turn, caustic pollutants create: Haze Corrodes paint and metals Poisons vegetation Creates unhealthful living and working conditions Contributes to lung cancer and other respiratory diseases Degrades aesthetic and property values

Table A-1-7
Sulfur Oxide Generation and Recovery in Western Smelters

Type of Smelter	Generated (long tons)	Recovered (long tons)	Percent Recovered
Copper Smelters	1,565,000	284,000	18.1
Zinc Smelters	440,000	165,000	37.5
Lead Smelters	160,000	42,000	26.3
All Smelters	2,165,000	491,000	22.7

Another serious source of mineral-industry-related air pollution is that generated by the numerous burning coal refuse banks. This condition results in the emission of smoke, dust, and poisonous and noxious gases which, in many instances,have proven fatal to surrounding human and vegetative life. The amount of identifiable gases taken from a burning coal refuse bank are listed in Table A-1-8. The Bureau of Mines has located and identified 291 burning banks, and 237 outcrop and mine fires in the United States (See Table A-1-9).

Table A-1-8
Analysis of Air Samples Taken from Two Boreholes in a Burning Coal Refuse Bank

Gases Identified	Percent of Gas Present	
Oxygen, O_2 ----------------------	7.6	1.0
Carbon Dioxide, CO_2 --------------	10.55	20.3
Carbon Monoxide, CO --------------	2.15	1.05
Ammonia, NH_4 --------------------	0.23	1.01
Nitrogen* -----------------------	79.47	76.64

* Determined by substracting percent of other gases from 100.

The location of the refuse sites frequently magnifies the serious effects from excessive concentration of these gases. Flames, thermal waves, smoke, fumes or a combination of all these characteristics were observed at the 292 burning coal waste piles. Of these, 260 banks are located less than five miles from a community of 200 and 13 coal heaps were less than one mile from these populated areas (Reference 6). A further delineation of the population of communities to burning coal waste piles is:

Number of Banks	Surrounding Population (each bank)
138	less than 1,000
123	1,001 - 10,000
25	10,001 - 100,000
6	more than 100,000

Table A-1-9
Environmental Damage of Underground and Surface Mining

State	No. of Burning Coal Refuse Banks	No. of Outcrop and Underground Mine Fires	No. of Communities Undermined	Accumulated Mineral Solid Wastes (millions of tons)	Acres of Unreclaimed Surface Mined Lands (thousands)	Acres of Lakes & Ponds Affected by Surface Mining
Alabama	6		1		83.0	16,300
Alaska		1		161.3	6.9	
Arizona		8	2	36.4	4.7	
Arkansas			4	38.2	16.6	200
California				437.5	107.9	74
Colorado	15	18	6	334.5	40.2	600
Connecticut					1.1	100
Delaware					3.5	200
Florida					143.5	
Georgia				11.7	13.5	390
Hawaii					**	
Idaoh			6	7.3	30.7	
Illinois	4		14	2.0	88.7	500
Indiana			22	2.5	27.6	
Iowa			6		35.5	
Kansas			23		50.0	50
Kentucky	29	4	2		79.2	100,000
Louisiana					17.2	100,000
Maine				7.8	21.6	
Maryland		2	2		18.1	72
Massachusetts					25.0	
Michigan			11	0.1	26.6	2,460
Minnesota			6	0.2	71.5	1,600
Mississippi					23.7	300
Missouri			56	96.0	43.7	6,000
Montana	3	39	3	28.5	19.6	
Nebraska					16.8	
Nevada			2	244.1	20.4	
New Hampshire					5.1	
New Jersey			6		21.0	
New Mexico		10		314.2	2.0	2
New York			3	67.9	50.2	100
North Carolina				8.7	22.8	
North Dakota		7			22.9	
Ohio	6	6	1*		171.6	120
Oklahoma	1		21		22.2	
Oregon			2		18.2	5.8
Pennsylvania	74	82	10	192.0	229.5	2,020
Rhode Island					2.2	
South Carolina					19.3	
South Dakota		1	1	105.8	25.3	9,275
Tennessee				1.2	62.5	100
Texas					136.4	
Utah	4	17		6.9	3.4	
Vermont				47.7	4.2	
Virginia	17	2	2	15.9	37.7	
Washington	1	1	1?	11.3	5.5	
West Virginia	132	16	10		111.4	4,683
Wisconsin			9	3.2	27.4	Trace
Wyoming		23	2		6.4	
TOTAL	291	237	252	2,201.1	2,040.6	

*Coal mines may underlie some urban areas in the southeastern portion of the State.

**Less than 1,000 acres.

Table A-1-10 details the amount of accumulated mineral industry solid waste (Reference 7).

4. Associated Hazards

The environmental hazards associated with wastes derived from the mining and processing of mineral ores are numerous, and are found throughout the entire process. Some of these hazards are as follows:

- Dust—This hazard accompanies every mining process and is responsible for uncomfortable, dirty, and hazardous working conditions. It fills and blackens the lungs of mine and mill employees. The resultant respiratory ailments are known as emphysema, black lung, silicosis, miners' lung, etc. Symptoms include loss of strength and vitality, inability to work, family hardships, and death. Dust concentrations in a small closed area are also subject to disasterous explosions.

- Waste Banks—Waste banks constitute a variety of hazards to people and the environment, depending on the wisdom displayed in the choice of sites. Many banks block small valleys or are being used to retain settling ponds. Flooding causes erosion and failure of the banks, ehdangering those who inhabit the vicinity of the waste. In many instances waste banks exceed the natural angle of repose for proper stability. The type of material determines the limits to this angle of repose. The effects of gravity strain the banks, the addition of water provides an increase in weight and acts as a lubricant, and when these effects exceed the limits of waste banks, dangerous slides may occur. Slides are also caused when people remove portions of the material for other uses, thus upsetting the bank stability.

Table A-1-10
Tonnage and Acreage of Accumulated Mineral Industry Solid Wastes

State	Antimony		Asbestos		Barite		Bauxite		Beryllium	
	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres
Alabama										
Alaska										
Arizona										
Arkansas					8.0	56	23.8	134		
California			30.0	180						
Colorado										
Connecticut										
Delaware										
Florida										
Georgia					2.0	400				
Hawaii										
Idaho	0.5	20								
Illinois										
Indiana										
Iowa										
Kansas										
Kentucky										
Louisiana										
Maine										
Maryland										
Massachusetts										
Michigan										
Minnesota										
Mississippi										
Missouri					96.0	430				
Montana					0.2	5				
Nebraska										
Nevada					4.0	30				
New Hampshire										
New Jersey										
New Mexico										
New York										
North Carolina										
North Dakota										
Ohio										
Oklahoma										
Oregon										
Pennsylvania										
Rhode Island										
South Carolina										
South Dakota									0.8	200
Tennessee					1.2	80				
Texas										
Utah										
Vermont			5.4	42						
Virginia										
Washington										
West Virginia										
Wisconsin										
Wyoming										

Table A-1-10
(Continued)

State	Boron		Clay		Coal		Copper		Diatomite	
	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres
Alabama					164.0					
Alaska					6.5	165	13.6	302		
Arizona						Acreage information not available	4764.0	20,500		
Arkansas					0.2					
California	76.0	600	18.0	475			30.0	1,100	64.0	740
Colorado					5.2					
Connecticut										
Delaware										
Florida										
Georgia			9.2	70	0.2					
Hawaii										
Idaho							2.0	90		
Illinois					222.4					
Indiana					62.8					
Iowa										
Kansas					12.3					
Kentucky					157.9					
Louisiana										
Maine					—		1.5	7		
Maryland					0.1					
Massachusetts										
Michigan					0.3		431.0	1,150		
Minnesota										
Mississippi										
Missouri					22.2					
Montana					0.8		930.0	5,500		
Nebraska										
Nevada							1346.0	9,000	11.5	85
New Hampshire										
New Jersey										
New Mexico					3.1		867.0	4,035		
New York										
North Carolina							0.8	15	75.5	825
North Dakota										
Ohio					84.4					
Oklahoma					1.9					
Oregon					0.1		0.4	35		
Pennsylvania					248.4					
Rhode Island										
South Carolina										
South Dakota										
Tennessee					2.3		3.0	100		
Texas										
Utah					10.4		2930.5	10,732		
Vermont										
Virginia					49.4					
Washington					10.0		12.5	140		
West Virginia					428.8					
Wisconsin										
Wyoming										

Table A-1-10
(Continued)

State	Feldspar		Fluorspar		Gold		Gypsum		Iron & Steel	
	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres
Alabama									188.6	696
Alaska					161.3	228				
Arizona					34.0	2200				
Arkansas										
California					122.0	840	16.5	100	86.7	640
Colorado			2.3	120	78.7	2715			20.2	121
Connecticut										
Delaware										
Florida										
Georgia									34.5	120
Hawaii										
Idaho					2.8	120			4.5	45
Illinois			2.0	40					84.7	
Indiana										
Iowa										
Kansas										
Kentucky										
Louisiana										
Maine										
Maryland									32.5	
Massachusetts										
Michigan									182.2	1326
Minnesota									389.7	5195
Mississippi										
Missouri									6.0	60
Montana					12.0	1500				
Nebraska										
Nevada					196.0	865	3.8	40	28.5	840
New Hampshire										
New Jersey									12.5	15
New Mexico			3.5	350	6.3	520			1.0	50
New York									290.6	1218
North Carolina	3.3	24								
North Dakota										
Ohio									193.4	1510
Oklahoma										
Oregon					5.5	200				
Pennsylvania									314.8	1738
Rhode Island										
South Carolina										
South Dakota	6.5	500			98.4	960				
Tennessee									23.2	10
Texas									28.8	
Utah					6.9	60			22.0	58
Vermont										
Virginia	0.1	2							3.1	14
Washington					4.2	175				
West Virginia									32.0	25
Wisconsin									6.0	35
Wyoming									28.5	280

Table A-1-10
(Continued)

State	Lead-Zinc-Silver Tons (millions)	Acres	Magnesite Tons (millions)	Acres	Manganese Tons (millions)	Acres	Mercury Tons (millions)	Acres	Mica Tons (millions)	Acres
Alabama										
Alaska										
Arizona	640.0	2000			2.0	40	0.1	30		
Arkansas										
California	9.3	85					21.0	420		
Colorado	330.0	5500			0.3	30				
Connecticut										
Delaware										
Florida										
Georgia										
Hawaii										
Idaho	153.5	3160								
Illinois	17.1	349					0.3	10	Amount Unknown	
Indiana										
Iowa										
Kansas	25.0	2250								
Kentucky										
Louisiana										
Maine										
Maryland										
Massachusetts										
Michigan										
Minnesota										
Mississippi										
Missouri	42.0	4600								
Montana	45.9	2160			3.4	100				
Nebraska										
Nevada			15.0	90	7.9	35	1.7	50		
New Hampshire										
New Jersey										
New Mexico	16.2	485			2.3	600				
New York										
North Carolina									5.4	45
North Dakota										
Ohio										
Oklahoma	101.8	5210								
Oregon							1.2	110		
Pennsylvania										
Rhode Island										
South Carolina										
South Dakota										
Tennessee	7.2	148								
Texas	12.0	70								
Utah	53.8	2385								
Vermont										
Virginia										
Washington	22.5	250	7.0	200						
West Virginia										
Wisconsin										
Wyoming										

Table A-1-10
(Continued)

State	Molybdenum		Miscellaneous		Nickel		Potash		Phosphate	
	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres	Tons (millions)	Acres
Alabama			161.3							
Alaska			161.3	228						
Arizona			36.4	2295						
Arkansas			38.2	215						
California			437.5	3780					3.4	56
Colorado	249.5	805	334.5	4180						
Connecticut										
Delaware									1.4	22
Florida									488.8	7566
Georgia			12.2	478						
Hawaii										
Idaho			7.3	450					47.0	230
Illinois			2.0	40					9.6	158
Indiana			2.5	100						
Iowa										
Kansas										
Kentucky										
Louisiana									5.5	91
Maine			7.8	114						
Maryland										
Massachusetts										
Michigan			0.1	2						
Minnesota			0.2	6					1.4	22
Mississippi									3.5	58
Missouri			96.0	430					2.6	42
Montana			28.5	1665					1.8	80
Nebraska										
Nevada			244.1	1232	11.5	150				
New Hampshire										
New Jersey										
New Mexico	68.0	849	314.5	3580			233.8	1143		
New York			67.9	405						
North Carolina			8.7	69					3.1	774
North Dakota										
Ohio									1.1	18
Oklahoma										
Oregon			18.2	460						
Pennsylvania			192.0	2553						
Rhode Island										
South Carolina										
South Dakota			105.8	1680						
Tennessee			1.2	80					38.6	590
Texas									7.3	121
Utah			6.9	60					1.4	20
Vermont			49.6	344						
Virginia			19.4	243						
Washington			11.4	395						
West Virginia										
Wisconsin			3.2	63						
Wyoming									0.1	10

Table A-1-10
(Continued)

State	Stone		Tungsten		Talc		Titanium		Vermiculite	
	Tons	Acres	Tons	Acres	Tons	Acres	Tons	Acres	Tons	Acres
Alabama										
Alaska										
Arizona			0.3	25						
Arkansas	6.4	25								
California	73.0	360	15.0	45	2.0	20				
Colorado			3.7	510						
Connecticut										
Delaware										
Florida										
Georgia										
Hawaii										
Idaho			3.7	300						
Illinois										
Indiana	2.5	100								
Iowa										
Kansas										
Kentucky										
Louisiana										
Maine	7.8	114								
Maryland										
Massachusetts										
Michigan	0.1	2								
Minnesota	0.2	6								
Mississippi										
Missouri										
Montana			0.9	40					12.0	20
Nebraska										
Nevada			3.9	35	0.3	2				
New Hampshire										
New Jersey										
New Mexico										
New York	4.9	75					63.0	330		
North Carolina										
North Dakota										
Ohio										
Oklahoma										
Oregon										
Pennsylvania	192.0	2553								
Rhode Island										
South Carolina										
South Dakota	0.1	20								
Tennessee										
Texas										
Utah										
Vermont	40.0	265			0.4	9				
Virginia	1.1	20					11.2	87		
Washington										
West Virginia										
Wisconsin	3.2	63								
Wyoming										

Table A-1-10
(Continued)

State	Grand Total Tons (millions)	 Acres	Remarks
Alabama	3526	696	
Alaska	3427	923	
Arizona	54768	27090	
Arkansas	766	430	
California	10049	9441	
Colorado	10244	13981	
Connecticut			
Delaware	14	22	
Florida	4888	7566	
Georgia	581	1068	
Hawaii			
Idaho	2216	4425	
Illinois	3378	587	
Indiana	2106	200	
Iowa			
Kansas	373	2250	
Kentucky	1579		
Louisiana	55	91	
Maine	171	235	
Maryland	326		
Massachusetts			
Michigan	6137	2480	
Minnesota	3915	5229	
Mississippi	35	58	
Missouri	2648	5562	
Montana	10355	11170	
Nebraska			
Nevada	18627	12454	
New Hampshire			
New Jersey	125	15	
New Mexico	15157	11614	
New York	4264	2028	
North Carolina	213	927	
North Dakota			
Ohio	2789	1528	
Oklahoma	1037	5210	
Oregon	369	805	
Pennsylvania	9472	6844	
Rhode Island			
South Carolina			
South Dakota	2116	3360	
Tennessee	764	1008	
Texas	481	191	
Utah	30319	13315	
Vermont	954	660	
Virginia	843	366	
Washington	676	1160	
West Virginia	4608	25	
Wisconsin	124	161	
Wyoming	286	290	

- **Waste Fires**—Burning waste banks constitute a case of potential instability during periods of heavy participation. Permeating water is converted in the presence of intense heat into watergas, which can and sometimes does explode violently, initiating debris slides.

  In addition, if the waste material is on fire, or thermally hot due to oxidation of pyritic material, it presents a danger to people in nearby communities. A number of tragedies have occurred in the United States in connection with waste bank fires (Table A-1-11). Burning banks also produce local smog conditions and contribute to living hazards as well as dangerous driving and flying conditions.

2. INDIVIDUAL MINERALS

Wastes associated with the mining of metals are of great volume for iron, copper, lead, zinc, and aluminum. Other important metals with lesser waste problems also warrant consideration in the study of waste, its control, and its subsequent effects on environmental pollution. The metals discussed in this section are categorized as follows:

.	SIC 101	Iron Ores
.	SIC 102	Copper Ores
.	SIC 103	Lead and Zine Ores
.	SIC 104	Gold and Silver Ores
.	SIC 105	Bauxite and Other Aluminum Ores
.	SIC 106	Ferroalloy Ores, Except Vanadium
.	SIC 109	Miscellaneous Metal Ores.

Table A-1-11
Deaths and Accidents Attributed to Coal Waste Fires
(partial list)

Year	Location	Remarks
1928	Iowa	An explosion while excavating a coal waste bank burned six men; three fatally.
1928	Iowa	An explosion while excavating a coal waste bank burned eleven men; three fatally.
1940's	Sagamore, West Virginia	Thirteen killed by an explosion of a burning coal refuse pile.
1940	Lochgelly, West Virginia	One killed by a slide while digging red dog.
1942	Oakwood, Virginia	Seven killed by an explosion and resultant slide of a bank.
1946	Virginia	Burning refuse bank ignited coal seam. Two killed by an explosion in the mine while investigating the extent of the fire.
1947	Alabama	Two killed while excavating burning refuse material.
1950	Mayberry, West Virginia	One child killed by falling through surface crust on a burning coal refuse pile.
1957(?)	Oakwood, West Virginia	Two killed by explosion while digging red dog.
1958	Sharples, West Virginia	Burning coal slide and covered mine opening; all men were rescued 48 hours later.
1960(?)	Hemp Hill, Kentucky	Two killed by asphixiation after falling into burning bank.
1960(?)	Rhoda, Virginia	Two killed by bank slide.
1966	Amherstdale, West Virginia	Explosion and resultant blank slide injured one child and destroyed several homes.

(1) SIC 101—Iron Ores

1. Description

Iron is the second most abundant element comprising about 5 percent of the solid rocks of the earth's crust. It is the most useful of metals because of its abundance and the ease with which it may be altered by adding small amounts of other elements. The U.S. is a major consumer of iron, requiring approximately 25 percent of the world's supply and producing about 13 percent of that supply.

2. Source and Production

The iron industry is widely distributed geographically. However, most production is centered in four principal areas: (1) Northeastern States of New York and Pennsylvania; (2) Lake Superior Region of Minnesota and Michigan; (3) Western States of Montana, Utah, and Wyoming; and (4) Southeastern States of Alabama and Georgia. The mines in these areas, together with 13 other states, were responsible for production of approximately 200 tons of crude ore in 1968, and processing took place in 18 of the states.

In this period there were 109 operating iron ore mines in the United States, 13 of which were underground. There were 175 integrated steel plants, 483 steel foundries, and 2,200 gray, malleable, and ductile iron foundries. Ore production was valued at $800 million, and revenues totaled $18.652 million.

3. Industrial Consumption

In 1968 the domestic availability of iron approximated 186.9 million short tons, utilized as follows:

Consumer	SIC Codes	Availability (short tons)	Article Use (%)
Transportation	371, 372, 373, 374	30.1	25
Construction Products	331, 343, 344	32.0	27
Machinery and Equipment	35, 252, 342, 361-2, 364-9	21.4	17
Containers	341, 349	7.9	7
Oil and Gas (pipe & equip.)	331, 353, 3443, 3586	5.6	5
Home appliance & equip.	251, 342, 363	6.1	5
Industry Stocks(as of 12/31/68)		56.3	
Exports		10.6	
Other		16.9	14

4. Future Outlook

Domestic steel averaged about 100 million short tons from 1964 through 1968; it is anticipated that there will be an annual growth rate of between 1.0 and 1.9 percent compounded. This indicates that the projected demand for iron for castings and steel finished products in the year 2000 will range between 162 and 221 million short tons.

5. Waste Characteristics

Waste products are generated at each stage of the steel conversion process; the most significant are mine waste, mill tailings, and furnace slags. Wastes accumulated by this industry up to 1968 exceeded 2 billion tons, covering approximately 14,000 acres of land, and is accumulating at the rate of 157 million tons per year in a 21-state area. A general breakdown in wastes includes:

- Mine Waste — Waste developed during the exploration, development, and mining of ore deposits. Approximately 190 million tons of mine waste, with an additional 500 million tons of lena ore found in 600 mine dumps, cover an estimated 6,600 acres.

- Mill tailings—This reject material is of three basic types: (1) clay, sand, and fine grained iron minerals from washing plants; (2) coarse and fine grained siliceous material from heavy-media, jig, and magnetic processes; (3) rejects from tocomite plants. Approximately 720 million tons of this waste exists, covering about 8,900 acres of land. The Lake Superior District is responsible for 80 percent of this material.

- Slag—The largest waste contributor in the iron and steel industry is of two types. The first type of slag is produced in the conversion of ore into the metal by means of the blast furnace. The waste products include metal slag, flue dust, scrap metal, and gas. About a half-ton of slag is produced per ton of pig iron. The second type of slag is produced when impurities are removed from the pig or scrap to produce grade steel. This type is a lesser problem than that generated by the blast furnace (Reference 8).

Approximately 1 billion tons of slag from both sources exist in piles covering over 3,700 acres of land; Pennsylvania and Ohio account for 3,000 acres of slag alone.

Flue dust from blast and steel furnace operations, is another significant pollution source. It is anticipated that it may exceed 3.5 million tons per year (Reference 9).

6. Associated Hazards

Inhalation of iron and iron oxides produces a benign siderosis (or pneumoniosis). In addition to the benign condition, there may be very serious synergistic effects as well as other undesirable effects, such as chronic bronchitis. In the laboratory, iron oxide acts as a vehicle to transport the carcinogens in high local concentrations to the target tissue. Similarly, sulfur dioxide is transported in high local concentrations deep into the lung by iron oxide particles. The relationships between these conditions and dose and time are undetermined. There is no apparent evidence of animal or plant damage.

Soiling of materials by airborne iron or its compounds may produce economic losses. For example, iron particles seem to produce stains on automobiles, requiring them to be repainted. Iron oxide particulates may also reduce visibility.

The results from the National Air Sampling Network showed that iron concentrations ranged up to 22 $\mu g/m^3$, with an average of 1.6 $\mu g/m^3$ in 1964. The most likely sources of iron pollution are from the iron and steel industry. The validity of this conclusion has been demonstrated by the decrease in iron concentration during steel strikes as well as by analysis of iron in the stack emissions. The iron pollution may be controlled by particulate removal equipment, such as electrostatic percipitators, venturi scrubbers, and filters.

Air pollution control cost the steel industry approximately $102 million in 1968. Fume control equipment costs for basic oxygen furnaces range between $3 and $7.5 million. This represents 14 to 19 percent of the total plant cost. Operating costs average $0.15 to $0.25 per ton of steel.

Further studies are suggested in the following areas:

- The role of iron and its compounds in carcinogenesis, especially at the low concentrations observed in the atmosphere.
- The role of iron and its compounds as synergistic agents with other air pollutants (such as sulfur dioxide) from at least two viewpoints: catalytic oxidation of pollutant in air and transport of pollutant into the lungs.
- The soiling characteristics of iron and its compounds as related to particle size, concentration, and chemical composition.

(2) SIC 102—Copper Ores

1. Description

Copper is one of the first metals used by humans because of its natural availability and the ease with which it can be worked to fashion utensils and weapons of lasting quality. Although the metal has a wide distribution in nature, there are relatively few large copper-producing areas in the world. The most important of these areas include: (1) Western United States; (2) Northern Michigan; (3) Western Canada; (4) West Slope of the Andes, Peru, and Chile; (5) Zambia and the Congo in Africa; and (6) Urul Mountains and Kazakston, Russia.

2. Source and Production

The United States has been the largest copper-producing country since 1883. Approximately 91 percent of domestic copper is produced in five Western States: Arizona, Montana, Nevada, New Mexico, and Utah, the remaining 9 percent is obtained from Michigan and Tennessee. In 1968, 25 mines accounted for 95 percent of the U.S. copper output, which was processed in 19 smelters. The major U.S. companies are vertically integrated and have mining, smelting, refining, and fabricating facilities and marketing organizations.

3. Industrial Consumption

In 1968 the domestic availability of copper approximated 3,615 thousand short tons, utilized as follows:

Consumer	SIC Code	Availability (short tons)	% Used
Electrical Equipment & Supplied	36	1,375	50
Construction	15, 16	445	16
Industrial Machinery (except elect.)	35	280	10
Transportation	37	335	12
Ordnance	19	172	6
Misc. (Jewelry, Chemical Pigments etc.)		204	7
Industry Stocks (as of 12/31/68)		563	
Exports		241	

Copper ore processing accounts for important quantities of gold, silver, molybdenum, nickel, selenium, tellurium, and arsenic, as well as iron, lead, zinc, and sulfur.

4. Future Outlook

In 1968 the world demand for copper continued high. In the U.S. the total demand for copper was only slightly above that of 1967 (2,811 thousand short tons and a total supply of 3,615 thousand short tons). Gains were made in foreign demand. It is anticipated that the average annual growth rates between 1968 and the year 2000 will range from 3.7 to 5.2 percent, which amounts to a demand in year 2000 of between 7.6 million to a high of 15.7 million tons.

5. Waste Characteristics

The copper production industy is considered to be the largest single source of solid waste because of the copper ore-metal yield ratio 130:1. This means that 99 percent of raw ore is rejected as waste, or about 170 million tons in 1968. Montana, Nevada, Utah, Arizona, New Mexico, and Michigan are the principal producers, and smelters in those states provide 40 percent of domestic refining capability.

The copper wastes, composed of mine waste, mill tailings, and smelter slags, now total 11.3 billion tons of waste, occupying 52,000 acres of land. These wastes accumulate at a rate of 492.6 million tons annually.

A general breakdown of copper wastes include:

- Mine Waste—Accounts for 54 percent of total waste generated largely from open pit operations in the five Western States. Improved leaching techniques will permit reprocessing of some of this ore for copper and by-products. This waste covers almost 23,000 acres of land.
- Mill Tailings—Five billion tons of this type of waste is impounded on over 28,000 acres of land surface.
- Copper Slag—Approximately 146 million tons of copper slag is presently disposed upon an area covering 1,400 acres.

(3) SIC 103—Lead and Zinc Ores

LEAD ORES

1. Description

Lead is one of the oldest metals used by man, and many of the ancient applications have persisted through to the present time. It is a soft, heavy metal, malleable but only slightly ductile, and is the most corrosion resistant of any of the common metals. Lead is widely used, alloyed with other metals. In tonnage produced, it ranks fifth behind steel, aluminum, copper, and zinc respectively.

2. Source and Production

Lead ores are derived from underground mining methods and beneficiated at mine sites. The concentrates are shipped to smelters and refineries for processing. During 1968 lead ores provided 64 percent of primary domestic lead, lead-zinc ores 26 percent, zinc ores 4 percent, and all other ores 6 percent. Missouri produced 60 percent, Idaho 14 percent, Utah and Colorado 13 percent each. The domestic requirements are supplied from domestic mine production, imported ore, imported metal, and domestic secondary.

3. Industrial Consumption

In 1968, the domestic availability of lead approximated 1.636 thousand short tons, utilized as follows:

Consumer	SIC Code	Availability (short tons)
Transportation	3691, 2911	762
General Building Construction	1511, 3432, 3341	250
Small Arms Ammunition	146	81
Packaging	3341, 3446	60
Communication equipment	366	87
Printing & publishing	27	32
Industry stocks	12/31/68	179
Exports		8
Other		177

The transportation industry was the major consumer of lead in 1968, accounting for 53 percent of the total demand. Most of this 53 percent was used in the manufacture of batteries and 18 percent was used as an additive for gasoline. Construction required 17 percent, although this area of lead use is declining. The communication industry is on the decline as a lead user. A slight increase in the use of lead is found in the small arms ammunition industry. The use of lead in packaging and publishing is declining, while the miscellaneous demand remains rather stable.

4. Future Outlook

The demand for lead in the United States in 1968 was 1,449 thousand short tons. The projected outlook for lead demand in the year 2,000 shows an average growth rate of 1.8 to 3.4 percent between 1968 and 2000. This would show a demand range between 2.52 to 4.4 million tons of lead, and indicates an increase in each industry producing end products of lead.

ZINC ORES

1. Description

The ores of zinc were used for making brass for centuries before it was recognized as a metal in 1746. It is a bluish-white metal, brittle at ordinary temperatures, but malleable at 100°C. The properties of being chemically active and alloying readily with other metals are utilized industrially in preparing a large number of zinc-containing alloys and compounds.

2. Source and Production

Most zinc is mined using underground mining methods, principally classed as open shrinkage, cut and fill, or square set stopping methods. There are 23 mines classified as zinc mines, 124 as lead-zinc mines, and 60 as lead mines. Oklahoma has the largest number of mines, 47, followed by Idaho with 34, and Colorado with 25. Tennessee, the leading producing state has 6 large mines. Twenty-one states produce zinc, with Tennessee producing more than 20 percent. New York, Idaho, Colorado, and Pennsylvania together with Tennessee produce more than 60 percent. A total of 7 companies produce more than 75 percent of domestic slab zinc output.

3. Industrial Consumption

In 1968 the domestic availability of zinc approximated 1,959 thousand short tons, utilized as follows:

Consumer	SIC Code	Availability (short tons)	% used
Construction	15, 16	340	19
Transportation	37	400	23
Electrical equipment & Supply	36	210	12
Plumbing and heating	3432, 3433	240	13
Industrial Machinery (exclud. elect)	35	160	9
Pigments & Compounds	2816, 2819	220	13
Rolled zinc, dry cells	2752, 3692	50	11
Industry Stocks (as of 12/31/68)		165	
Exports		33	
Other		141	

4. Future Outlook

The 1968 demand in the United States for lead metal amounted to 1, 761 thousand short tons. The projected outlook for zinc requirements in the year 2000 is based on forecasted annual growth rates of between 1. 1 percent to 3. 1 percent, converted into a projected zinc demand of between 2. 46 million tons to 4. 7 million tons as compared to the 1968 demand.

5. Lead Zinc Wastes Characteristics

It is estimated that, since the advent of lead-zinc mining in the U.S., this industry has accounted for more than 1.5 billion short tons of crude ore, containing 35.2 million tons of zinc and 31.6 million tons of lead. The three categories (1) mine waste, (2) jig and flotation mill tailings, and (3) refining slag, accounted for 93 percent of the total solid waste covering 45 square miles of surface area (see Table A-1-12).

- Mine Waste—There is presently approximately 700 million tons of boulder piles and rock dumps covering 15,000 acres associated with lead-zinc mines. At the current production level, an estimated 3. 5 million tons of mine waste will be added annually. Some waste piles 40 years

Table A-1-12
Estimated Magnitude of Solid Waste Accumulations for Lead-Zinc-Silver

State and Type of Solid Waste	Accumulated through 1968 (thousand tons)	Acres
Arizona		
Mine waste	319,000	1,100
Mill tailings	319,000	700
Smelter slag	2,000	200
California		
Mine waste	2,300	30
Mill tailings	6,000	50
Smelter slag	1,000	5
Colorado		
Mine wastes	275,000	5,000
Mill tailings	55,000	500
Smelter slag	-------	-----
Idaho		
Mine-mill-smelter	153,450	3,160
Illinois-Wisconsin		
Mine waste	1,000	25
Mill tailings	16,050	320
Smelter slag	18	4
Kansas		
Mine waste	3,730	2,250
Mill tailings	21,220	
Smelter slag		
Missouri		
Mine waste	8,860	4,600
Mill tailings	33,110	
Smelter slag		
Montana		
Mine-mill-smelter	45,900	2,160

Table A-1-12
(Continued)

State and Type of Solid Waste	Accumulated through 1968 (thousand tons)	Acres
New Mexico		
Mine waste	1,000	8
Mill tailings	15,000	465
Smelter slag	200	12
New York		
Mine waste		
Mill tailings		
Smelter slag		
Oklahoma		
Mine waste	1,190	5,210
Mill tailings	100,570	
Smelter slag	-----	
Pennsylvania		
Mine waste		
Mill tailings		
Smelter slag		
Tennessee		
Mine waste	-----	-----
Mill tailings	7,150	148
Smelter slag	-----	-----
Texas		
Smelter slag	12,000	70
Utah		
Mine waste	28,700	1,840
Mill tailings	14,500	345
Smelter slag	10,600	200
Washington		
Mine waste	2,500	50
Mill tailings	20,000	200
Smelter slag	-----	-----
Total	1,476,048	28,652

old still do not support vegetation due to sulfur contents. This pollutant limits the reclamation of mine wastes.

- Jig and Flotation Tailings— Lead and zinc ores are crushed and ground to permit recovery of metals. To date there are in existence 740 million tons of mill wastes covering 13,000 acres. Siliceous dust from dry lead zinc tailing ponds menaces health and comfort of nearby communities. Again sulfide contents limit the reclamation of mill tailing wastes.

- Slag— Production of lead and zinc metal has resulted to date in nearly 32 million tons of smelter wastes, covering approximately 2,500 acres of the earth's surface. Most slag is being retreated at fuming plants to recover additional lead and zinc. Slag wastes are accumulating at a rapid rate as shown in Table A-1-12.

6. Associated Hazards

It is not possible to assess fully the role of zinc and its compounds as air pollutants. Despite the fact that specific effects attributable to certain compounds of zinc have been noted, the common association of zinc with other metals, and the frequent presence of toxic contaminants (such as cadmium) in zinc materials, raise questions which have yet to be answered concerning the synergistic effects of these metals.

The most common effects of zinc poisoning in humans are nonfatal metal-fume fever, caused by inhalation of zinc oxide fumes, and illnesses arising from the ingestion of acidic foods prepared in zinc-galvanized containers. Zinc chloride fumes, though only moderately toxic, have produced fatalities in one instance of highly concentrated inhalation. Zinc stearate has been mentioned as a possible cause of pneumonitis. Zinc salts, particularly zinc chloride produce dermatitis upon contact with the skin.

Accidental poisoning of cattle and horses has occurred from inhalation of a combination of lead- and zinc-contaminated air. Zinc oxide concentrations of 400 to 600 $\mu g/m^3$ are toxic to rats, producing damage to lung and liver, with death resulting in approximately 10 percent of the cases. Although dogs and cats tolerate high concentrations (up to 1,000,000 μg/day) of zinc oxide for long periods, glycosuria and damage to the pancreas may result. Concentrations of 40,000 to 50,000 $\mu g/m^3$ of zinc ammonium sulfate produce no appreciable effects on cats.

Some evidence exists of damage to plants from high concentrations of zinc in association with other metals. No information was found on damage to materials from zinc or its compounds in the atmosphere.

The primary sources of zinc compounds in the atmosphere are the zinc-, lead-, and copper-smelting industries, secondary-processing operations which recover zinc from scrap are brass-alloy manufacturing and reclaiming, and galvanizing processing. Average annual production and consumption of zinc in the U.S. have increased steadily during this century, and it is predicted that this trend will continue. As the emission of zinc into the atmosphere, in most of these operations, represents an economic loss of the zinc material, control procedures are normally employed to prevent emission to the atmosphere. In those industries where zinc is a by-product, control procedures for zinc are not as effective, and greater quantities of zinc therefore escape into the environment.

Measurement of the 24-hour average atmospheric concentrations of zinc in primarily urban areas of the United States reveal an average annual value of 0.67 $\mu g/m^3$

for the period 1960-1964; the highest value recorded during that period was 58.00 $\mu g/m^3$, measured in 1963 at East St. Louis, Illinois.

Extensive air pollution abatement methods are in general use by the zinc industry. Control devices include precipitator scrubbers, baghouses, and collectors. The efficiency of the various control methods varies widely. However, in many instances air pollution control devices are not used in the general metals industries. Thus, at present, relatively large quantities of zinc or zinc compounds are still being emitted into the atmosphere by industrial plants processing zinc or other compounds containing zinc. No information has been found on the economic costs of zinc air pollution or on the costs of its abatement.

Limited means are available for the determination of concentrations of zinc in the ambient air. These methods of analyses, however, are not considered adequate for air pollution monitoring purposes since they do not effectively discriminate between the zinc and other metals and they lack sensitivity.

Further studies are suggested in the following areas:

- **Determination of whether zinc acts either as an individual air pollutant exerting specific effects or as a co-pollutant exerting synergistic effects, or has no adverse effects.**
- **Determination of which zinc compounds are present as pollutants in the environmental air, together with the manner in which—and extent to which—these substances effect human, animal, and plant life.**

(4) SIC 104—Gold and Silver Ores

GOLD

1. Description

Gold is widely distributed, mostly in the metallic state, and is one of the first metals used by man. It is the most malleable and ductile, and also one of the softest of metals. It is a good conductor of electricity and heat, and is not affected by air and most reagents.

2. Source and Production

At the present time about two-thirds of the gold produced comes from gold ore and placer mines. The remaining third is recovered from copper and other base metals. Three leading good producing mines—two gold mines, and one copper mine—account for 75 percent of total output.

3. Industrial Consumption

The 1968 total domestic availability of gold was 45.4 million troy ounces, with an industrial demand of 8 million troy ounces, as shown in Table A-1-13. Major uses are jewelry, precious metals, dental equipment, and electronic components.

4. Future Outlook

The projected annual growth rate for gold demand between 1968 to the year 2000 has been set between 3.4 and 4.8 percent. This converts to a volume demand of between 23.1 to 36.5 million troy ounces.

5. Waste Characteristics

Gold industry related wastes have accumulated to a point where 15 square miles of land have been covered. The breakdown is as follows:

- Mine waste - 327 million tons, covering 4,668 acres

Table A-1-13
Estimated Magnitude of Solid Wastes Accumulations from Gold

State and Type of Solid Waste	Accumulated thru 1968		1967	
	Tons (thousands)	Acres	Tons (thousands)	Acres
Alaska				
Mine waste	67,300	108		
Mill tailings	94,000	120		
Smelter slag	-----	---		
Total	161,300	228		
Arizona				
Mine waste	22,000	1,200	Insignificant	
Mill tailings	10,000	800		
Smelter slag	2,000	200		
Total	34,000	2,200		
California				
Mine waste	32,000	200	Less than	
Mill tailings	90,000	640	1,000 tons	
Smelter slag				
Total	122,000	840		
Colorado				
Mine waste	26,000	1,200	Insignificant	
Mill tailings	47,650*	1,315		
Smelter slag	5,000	200		
Total	78,650	2,715		
Idaho				
Mine waste and Mill tailings	2,800	120	NA	
Smelter slag				
Total	2,800	120		
Montana				
Mine waste and Mill tailings	12,000	1,500	NA	
Smelter slag				
Total	12,000	1,500		

NA = Not Applicable

* = Data includes 16 million tons of tailings covering 215 acres at Old Golden Cycle Mill, later used for residential complex.

Table A-1-13
(Continued)

State and Type of Solid Waste	Accumulated thru 1968		1967	
	Tons (thousands)	Acres	Tons (thousands)	Acres
Nevada				
Mine waste	149,000**	615	7,000	21
Mill tailings	47,000	250	1,300	6
Smelter slag				
Total	196,000	865	8,300	27
New Mexico				
Mine waste	5,000	100	Insignificant	
Mill tailings	1,000	400		
Smelter slag	250	20		
Total	6,250	520		
Oregon				
Mine waste	500	100		
Mill tailings	5,000	100	1,000	
Smelter slag				
Total	5,500	200	1,000	
South Dakota				
Mine waste	20,000	250		
Mill tailings	72,240	695	400	20
Smelter slag	6,190	15		
Total	98,430	960	400	20
Utah				
Mine waste	2,300	35	Insignificant	
Mill tailings	4,600	25		
Smelter slag				
Total	6,900	60		
Washington				
Mine waste	750	50		
Mill tailings	3,400	125	200	2
Smelter slag				
Total	4,150	175	200	2

**Includes about 125 million tons from open-pit operations.

.	Tailing waste	-	384 million tons, covering 5,280 acres
.	Smelter slag	-	13 million tons, covering covering 435 acres.

SILVER

1. Description

Silver normally occurs in deposits associated with other metals, such as copper, lead, zinc, and gold. It is pure white with a brilliant luster, a little harder than gold but only slightly less malleable and ductile.

2. Source and Production

In 1968, about two-thirds of the domestic silver output came from ores mined chiefly for copper, lead, and zinc. The remaining third was recovered from ores in which zinc was the principal metal. Half the domestic supply came from seven mines in the Coeurd'Alene mining district in the Idaho panhandle. Other source areas include Utah, Arizona, and Montana.

3. Industrial Consumption

The 1968 total domestic availability of silver was 628.8 million troy ounces, with a demand of 182.1 million troy ounces. The heaviest consumers of silver are silverware and silver plate, photographic equipment, coinage, with jewelry, refrigeration, household appliances, batteries, switchgear, etc., using somewhat lesser amounts.

4. Future Outlook

The projected annual growth rate for silver demand in the period 1968 to 2000 is 1.4 to 3.6 percent, which, when translated to volume, amounts to between 280 to 560 million troy ounces.

5. Waste Characteristics

The silver wastes together with lead and zinc wastes are shown in Table A-1-12 (see page A-1-44).

(5) SIC 105 — Bauxite and Other Aluminum Ores

1. Description

Aluminum is the most abundant metallic element in the earth's crust, and ranks third among the elements. However, it does not appear in a free state. It is found as the silicate in clays, feldspars, etc., while the commercial ore at present is bauxite, an impure hydrated oxide. It ranks second among metals in the scale of malleability, and sixth in ductility. The oxide, alumina, occurs naturally as ruby, sapphire, corundum, and emery, and is very hard, ranking next to the diamond. The use of aluminum exceeds the use of any other metal in quantity or value except steel, and its growth rate has been about three times as great as other metals.

2. Source and Production

The U. S. is the leading producer of aluminum, producing 37 percent of the 1968 world total. About 95 percent of the bauxite produced domestically comes from Arkansas, and is processed into alumina at the mines. The remainder comes from Alabama and Georgia. In addition, approximately 86 percent of the bauxite consumed annually in the U.S. is imported primarily from Jamaica and Surinam. Alumina produced in 1968 at eight plants located in Alabama, Arkansas, Louisiana, and Texas, amounted to 6.4 million tons, requiring 13.2 million tons of bauxite and over 6.5 million tons of alkaline mud waste. Reduction plants more widely dispersed include Oregon and Montana (10 plants); West Virginia, Ohio, and Indiana (3 plants); Tennessee, Alabama, and North Carolina (4 plants); and New York (2 plants). Three of the largest aluminum companies account for 76 percent of primary aluminum in 1968. The remaining five domestic producers of primary metal also own finished aluminum product facilities.

3. Industrial Consumption

In 1968 the domestic availability of aluminum metal approximated 6,954 thousand short tons, utilized as follows:

Consumer	SIC Code	Availability (short tons)	% Used
General Building Contractors	1511	1,000	23
Motor Vehicles	371	670	10
Aircraft Parts	372	165	4
Ship & Boat Bldg and repair	373	20	3
Railroad Trans.	40	18	3
Electrical Equip. and supplies	36, 3352	600	14
Fabricated Metal Prods.	34	470	11
Machinery (except electric)	35	310	14
Metal Cans.and containers	3411	460	11
Highway & Street Construction	1611	60	1
Other Manufacturing	399	530	2
Abrasives aluminous	3291	80	1
Chemical & Allied products	28	160	1
Non Clay refractories	3297	162	1
Industry Stocks (as of 12/31/68)		1,441	
Exports		808	

Aluminum is in competition with copper, steel, tinplate, magnesium, lead, wood, plastics, and fiberglass.

4. Future Outlook

The 1968 demand in the U.S. for aluminum amounted to 4,705 thousand short tons. The projected outlook for aluminum requirements for the year 2000 is based on an annual growth rate of between 5.1 percent and 7.4 percent. This converts into a projected aluminum demand of between 21.2 million and 42 million tons.

5. Waste Characteristics

Each of the three types of bauxite (Jamaica, Surinam, and domestic) used to produce alumina yields a waste with significantly different physical and chemical properties requiring different procedures for disposal. The Jamaica and Surinam bauxite produces metal by the Bayer process, where aluminum is dissolved from bauxite with caustic soda. The residue "red mud" is retained in settling ponds. The "red mud" from domestic bauxite retains appreciable amounts of alumina, which is removed with lime and soda ash (combination process). This residue, called "brown mud", is also pumped into settling ponds.

About 3.6 million tons, of over 6.5 million tons of alkaline muds generated annually, are kept in ponds. The remaining 2.9 million tons are discharged into the Mississippi River. Accumulation of muds over the last 20 years have increased by 8 percent per year (Table A-1-14). Reclamation is difficult; however, 80 percent of the solids can be filtered out of the mud wastes.

(6) SIC 106—Ferroalloy Ores, Except Vanadium

The following metals are included in this section:

- Manganese
- Tungsten
- Chromium
- Colbalt
- Molybdenum
- Nickel.

MANGANESE

1. Description

Mananese is a metal resembling chromium and iron, and is essential for the economical production of cast iron and steel. This use of manganese far exceeds any other use.

Table A-1-14
Accumulated Mud Wastes from Alumina Refining

Type of Muds	Type of Bauxite	Accumulated 1942 - 65 (Thousand Tons)		Generated 1966 - 67 (Thousand Tons)		Accumulated 1942 - 67 (Thousand Tons)	
		Dry Basis	Wet Settled	Dry Basis	Wet Settled	Dry Basis	Wet Settled
Red Muds							
Alabama							
Mobile	Surinam	6,500	13,000	1,000	2,000		
Total Alabama		6,500	13,000	1,000	2,000	7,500	15,500
Louisiana							
Burnside	Surinam	1,000	2,000	430	860	1,430	2,860
Baton Rouge*	Jamaica	—	—	2,120	—	—	—
Gramercy*	Jamaica			1,260			
Total Louisiana		1,000	2,000	3,810	860	1,430	2,860
Texas							
LaQuinta	Jamaica	9,000	22,500	1,880	4,700		
Point Comfort	(Jamaica) (Surinam)	3,500	8,750	1,820	4,500		
Total Texas		12,500	31,250	3,700	9,200	16,200	40,450
Brown Muds (including 15%-18% sand)							
Arkansas							
Bauxite	Domestic	5,000	8,300	650	1,080		
Hurricane Creek	(Domestic) (Jamaica) (Surinam)	9,000	15,000	1,120	1,860		
Total Arkansas		14,000	23,300	1,770	2,940	15,770	26,240
Inoperative plants							
Illinois							
East St. Louis	Surinam	2,000	4,000			2,000	4,000
Total Generated				10,280			
Total Deposited in Mud Lakes		36,000	73,550	6,900	15,000	42,900	88,550

* Discharged into Mississippi River

2. Source and Production

The manganese industry in the United States processes mostly imported manganese ores, since less than 4 percent of the domestic manganese requirement is recovered from domestic ores. About 90 percent of the ores are produced by 10 companies in 15 plants. The domestic source of low grade ores include Montana, Colorado, New Mexico, and Minnesota.

3. Industrial Consumption

In 1968 the total availability of manganese approximated 2, 357 thousand short tons, with a domestic demand of 1, 180 thousand short tons (Table A-1-15). Nearly 25 percent of the manganese was consumed in production of cast iron and steels; transportation, machinery and equipment required 17 percent; home appliances, furniture and pipes and tubing used 15 percent; chemicals, batteries and other uses accounted for the rest of the manganese demand.

Table A-1-15
Industrial Consumption Chart

SIC	Description / Ferrous Minerals	Manganese (1000 S.T.)	Tungsten (1000 lb)	Chromium (1000 S.T.)	Cobalt (1000 lb)	Molybdenum (Mil. lb)	Nickel (Mil lb)
15	Construction (Building)			116			20.6
16	Construction (Nonbuilding)						
28	Chem. Anal. Pigments etc.	59				4.5	67.6
29	Petrolium Refining						
32	Ceramics	see (28)			300		
33	Primary Metals	651		75		23.4	
34	Containers						49
35	Machinery Nonelect.			79			25.1
36	Machinery Elect.	15	650*		3654	1.4	40.4
37	Transportation	273	2500*	85		16.5	
281	Misc. Chem. Products				1576		
331	Blast Furnaces, Steel Works						
334	Secondary Smelting						
342	Cutlery, Hand Tools						
344	Fabricated Structural Prod.						
353	Construct & Related Mach.		2950*		849		
354	Metalworking Machinery		8250*				
363	Home Appliances & Equip.			28			36.3
371	Motor Vehicles & Equip.						44.0
372	Aircraft Parts.						48.5
373	Ship & Boat Building						18.2
2816	Inorganic Pigments			16			
2819	Industrial Chemicals		450*				
2851	Paint & Allied Products				1179		
3111	Leather Products			11			
3297	Non-Clay Refractories			see (33)			
3471	Plating of Metals			22			
3479	Coating & Engraving			see (2816)			
3541	Machine tools				906		
3641	Lamps		950*				
3722	Aircraft Eng. Parts				3,667		
	Industry Stocks	1,180	8,287	345	5,888	37.9	74.4
	Exports & Other	179	1,123	131	3,431	39.9	54.2
	Total	2,357	25,160	908	21,459	123.6	478.4

*Estimated

4. Future Outlook

The projected annual growth rate for manganese between 1968 and the year 2000 is averaged at 2.25 percent. The demand volume of metal for the year 2000 is expected to range between 1.8 and 2.3 million tons.

5. Waste Characteristics

Solid wastes produced by the manganese industry to date amount to approximately 15.8 million tons, covering about 805 acres of land surface. An estimated 3 tons of rock are derived from each ton of ore produced. Process or concentrate tailings are currently marketed in Canada, hence are not accumulating. Estimated manganese wastes (Reference 10) are shown in Table A-1-16.

6. Associated Hazards

Inhalation of manganese oxides may cause chronic manganese poisoning or manganic pneumonia. Chronic manganese poisoning is a disease affecting the central nervous system, resulting in total or partial disability if corrective action is not taken. Some people are more

Table A-1-16
Estimated Magnitude of Solid Waste Accumulations for Manganese

State and Type of Solid Waste	Accumulated thru 1968	
	Tons (thousands)	Acres
Arizona		
Mine waste	2,000	40
Mine tailings		
Smelter slag		
Total	2,000	40
Colorado		
Mine waste	250	30
Mill tailings		
Smelter slag		
Total	250	30
Montana		
Mine waste	3,400*	100*
Mill tailings		
Smelter slag		
Total	3,400	100
Nevada		
Mine waste	6,200	25
Mill tailings	1,700	10
Smelter slag		
Total	7,900	35
New Mexico		
Mine waste	2,250*	600*
Mill tailings		
Smelter slag		
Total	2,250	600

* Total of mine waste and mill tailings.

susceptible to manganese poisoning than others. Manganic pneumonia is a croupous pneumonia often resulting in death. The effect of long exposure to low concentrations of manganese compounds has not been determined.

Manganese compounds are known to catalyze the oxidation of other pollutants, such as sulfur dioxide, to more undesirable pollutants—sulfur trioxide, for example. Manganese compounds may also soil materials.

The most likely sources of manganese air pollution are the iron and steel industries producing ferromanganese. Two studies, one in Norway and one in Italy, have shown that the emissions from ferromanganese plants can significantly affect the health of the population of a commuity. Other possible sources of manganese air pollution are manganese fuel additives, emissions from welding rods, and incineration of manganese-containing products, particularly dry-cell batteries. Manganese may be controlled along with the pariculates from these sources. Air quality data in the United States showed that the manganese concentration averaged 0.10 $\mu g/m^3$ and ranged as high as 10 $\mu g/m^3$ in 1964.

No information was found on the economic costs of manganese air pollution or on the costs of its abatement.

Further studies in the following areas are suggested:

- The effect of inhalation over varying periods of time of low concentrations of the manganese compounds found in the atmosphere.
- The chemical composition and particle-size distribution of the manganese compounds in the atmosphere.
- The effect of managanese air pollution on commercial plants and animals.
- Measurement of the concentration of manganese both near suspected sources and as emitted from suspected sources.
- The economic losses due to mananese air pollution.

TUNGSTEN

1. Description

Tungsten is a heavy, hard, heat-resistant metal. At high temperatures (above 3,000°F), it outranks all other metals in tensile strength. It is chracterized by good corrosion resistance, good electrical and thermal conductivity, and low thermal expansion coefficient. Major industrial application include its use in cutting and shaping other metals, in alloys, as filaments in electric lamps, and in ceramics.

2. Source and Production

Most of the tungsten produced in the U.S. in 1968 was recovered as a co-product of molybdenum operations. Tungsten mines produced minor quantities of co-product copper, gold, and silver. Most tungsten concentrate is produced from about 50 mines, most of it derived from the Pine Creek Mine of Union Carbide Corp. in California where tungsten is the major product, and the Climax Mine in Colorado where tungsten is the secondary product. The U.S. consumes about 20 percent of the world's metal.

3. Industrial Consumption

The 1968 total United States availability of tungsten was 25,160 thousand pounds utilized as shown in Table A-1-15. The major domestic users of tungsten include: metalworking machinery, which required 50 percent of the total consumption; construction, and mining machinery and equipment requiring 18 percent; transportation industry, approximately 15 percent; electrical lamps and other electrical equipment, about 10.5 percent; with chemicals and others using the remaining 6 percent.

4. Future Outlook

The projected annual growth for the tungsten industry demands between 1968 and the year 2000 has been set at between 4.2 and 5.6 percent. This projection converts to a volume of between 60 and 93 million pounds.

5. Waste Characteristics

Solid wastes generated by the tungsten industry presently total over 12.3 million tons of coarse material and 15.9 million tons resulting from upgrading and milling. The combined tungsten-related mine and mill wastes currently cover about 955 acres of land (Reference 10), as shown in Table A-1-17.

Table A-1-17
Estimated Magnitude of Solid Waste Accumulations for Tungsten

State and Type of Solid Waste	Accumulated thru 1968		1967	
	Tons (thousands)	Acres	Tons (thousands)	Acres
Arizona				
Mine waste	200	15	Insignificant	
Mill tailings	50	10		
Smelter slag				
Total	250	25		
California				
Mine waste	5,000	10		
Mill tailings	10,000	35	350	2
Smelter slag				
Total	15,000	45	350	2
Colorado				
Mine waste	3,500	500	Insignificant	
Mill tailings	200	10		
Smelter slag				
Total	3,700	510		
Idaho				
Mine waste	2,500	300	20	3
Mill tailings	1,200*			
Smelter slag				
Total	3,700	300	20	3
Montana				
Mine waste	850**	40**	Insignificant	
Mill tailings				
Smelter slag				
Total	850	40		
Nevada				
Mine waste	300	5	Inactive	
Mill tailings	3,600	30		
Smelter slag				
Total	3,900	35		
Utah				
Mine Waste				
Mill tailings				
Smelter slag				
Total				

* = Tailings used for airstrip base ** Total of mine waste & tailings

CHROMIUM

1. Description

Chromium is a steel gray metal prepared by electrolysis from one of several chromium-containing electrolytes, or by using the aluminothermic process. Chromium is chiefly used in alloy form, principally with iron. Chromite is the only commercial chromium mineral, and contains varied amounts of its oxides, iron aluminum, and magnesium. It exists in three grades (metallurgical, refractory, and chemical), depending largely on chromium content.

2. Source and Production

Chromite has not been mined in the U.S. since 1961, therefore, the domestic industry is depended on foreign supply. The three industries: metallurgical, refractory and chemical consume about 25 percent of the world's supply. In 1968, seven companies in 12 locations produced all the metal alloys. There were 11 principal refactory producers and four large chemical producers. Chromite was imported from the U.S.S.R., Republic of South Africa, Turkey, the Philipines, and Albania, with the U.S.S.R. and South Africa supplying 75 percent.

3. Industrial Consumption

In 1968, total availability of chromium was 908 thousand short tons, utilized as shown in Table A-1-15 (page A-1-63) with the domestic demand being 505 thousand short tons. The metallurgical companies required approximately 67 percent of the total demand, the refractory industry consumed 18 percent, and about 15 percent was used in the chemical industry.

4. Future Outlook

The projected annual growth rate for chromium between 1968 and the year 2000, falls between 2.0 and 3.3 percent, which implies a metal volume between 985 and 1,427 thousand short tons.

5. Waste Characteristics

The only environmental problems are those of processing; no ore is mined domestically. All major producers use control measures to control pollution effects of the OH gases produced during processing.

6. Associated Hazards

The exposure of industrial workers to airborne chromium compounds and chromic acid mists, particularly the hexavalent chromates, has been observed to produce irritation of the skin and respiratory tract, dermatitis, perforation of the nasal septum, ulcers, and cancer of the respiratory tract. Chromium metal is thought to be non-toxic. Hexavalent compounds appear to be much more harmful than trivalent compounds, with the toxic effects depending on solubility. Two effects that appear to be particularly important in relation to air pollution are hypersensitivity to chromium compounds and induction of cancers in the respiratory tract. Exposure of industrial workers in the chromate-producing industry has shown an incidence of deaths from cancer of the respiratory tract which is over 28 times greater than expected. Time-concentration relationships for induction of cancer are not known.

No evidence of damage by airborne chromium to animals or plants has been found. Chromic acid mists have discolored paints and building materials.

In 1964, atmospheric concentrations of total chromium averaged 0.015 $\mu g/m^3$ and ranged as high as 0.350 $\mu g/m^3$. Although the exact sources of chromium air pollution are not known some possible sources are the metallurgical, refractory, and chemical industries that consume chromite ore, chemicals and paints containing chromium, and cement and asbestos dust. Particulate control methods should be adequate for chromium-containing particles.

No information has been found on the economic costs of chromium air pollution or on the costs of its abatement. Methods of analysis are available to determine the amount of chromium concentration in the ambient air.

Further studies are suggested in the following areas:

- Resolution of the question of toxicity, hypersensitivity, and cancer induction with relation to the valence of chromium and solubility of chromium compounds.
- Determination of the concentration and time of exposure of chromium required to produce cancer.
- Determination of the concentration and time of exposure of chromium required to produce allergenic reactions in hypersensitive people of the general public.

- Determination of the concentration and valence of chromium adjacent to chrome steel plants, refractory fabricating plants, chromate-producing plants, chrome-plating operations, spray-painting operations, cement-making operations, etc.

COBALT

1. Description

Cobalt is one of the refractory metals of the space age, and is widely used in electronic devices and certain paints and ceramics. It is essential in machine tools, carbides, and high strength permanent magnets.

2. Source and Production

The U.S. produces only a small quantity of cobalt, and relies principally on imports for its supply of primary cobalt. The U.S. annually produces 500 to 600 short tons, and it is the principal user of cobalt.

3. Industrial Consumption

In 1968, the total domestic availability of cobalt was 21,459 thousand pounds, the demand being 14,151 thousand pounds, utilized as shown in Table A-1-15 (page A-1-63).

About 25 percent was used in aircraft and space; 20 percent consumed in electrical equipment; a little more than 20 percent used in paints, ceramics, chemicals, etc.; and 10 percent in tools and related machines.

4. Future Outlook

The projected annual growth rate for cobalt demand, between 1968 and the year 2000, is set between 1.0 and 2.4 percent, which means that about 18.64 to 30.54 million pounds of cobalt will be required by the year 2000.

5. Waste Characteristics

The solid wastes associated with the production of cobalt are insigificant, since only a small amount is produced domestically.

MOLYBDENUM

1. Description

Molybdenum is a silvery-white metal and is malleable and ductile when hot. Molybdenite is the principal source of this metal. It is also found as a by-product or co-product in the processing of other molybdenum-bearing ores.

2. Source and Production

Molybdenite was mined at three deposits by two companies in 1968. The largest producer of the metal produces concentrate at Climax and Urad, Colorado, while the second largest produces concentrate at Questa, New Mexico. Approximately 25 percent of the domestic molybdenum in 1968 derived from molybdenum-bearing copper, tungsten, and uranium ores, the bulk being from copper. Nine other companies produce molybdenum as a by-product. One ton of commercial molybdenum ore will produce from 2 to 6 pounds of metal.

3. Industrial Consumption

The 1968 total United States availability of molybdenum was 123.6 million pounds, with an industrial demand of 55.8 million pounds, utilized as shown in Table A-1-15 (page A-1-63). The U.S. produced about 75 percent of the world's supply. The transportation industry accounted for about 30 percent of the total demand, with about 25 percent required for production of commercial machinery and equipment. The pipe and tubing industry accounted for 18 percent of the total, and chemicals, catalytic, pigment, and lubricants used 8 percent, electrical and electronic compounds utilized 3 percent, and other industries required the remainder.

4. Future Outlook

The projected annual growth for molybdenum demand, between 1968 and the year 2000, has been set at approximately 4 percent. This implies an estimated volume of between 151 and 207 million pounds in the year 2000.

5. Waste Characteristics

The accumulation of mine wastes through 1968, total over 58 million tons. Mill wastes account for 258 million tons covering an estimated 819 acres. At the present time there exists nearly 320 million tons of industry-related solid waste, covering 1,654 acres of land. An estimate of accumulated waste per year is in excess of 15.5 million tons (Table A-1-18).

Table A-1-18
Estimated Magnitude of Solid Waste
Accumulations for Molybdenum

State and Type of Solid Waste	Accumulated thru 1968 Tons (thousands)	Accumulated thru 1968 Acres	1967 Tons (thousands)	1967 Acres
Colorado				
Mine waste	1,250	25		
Mill tailings	248,250	780	15,500	60
Smelter slag				
Total*	249,500	805	15,500	60
New Mexico				
Mine waste	57,500	810	25,000	400
Mill tailings	10,500	39	3,500	10
Smelter slag				
Total**	68,000	849	28,500	410

* Total for two underground molybdenum mines
** Total for one open-pit molybdenum mine

NICKEL

1. Description

Nickel is an extremely hard and brilliant metal, which is resistant to actions of the atmosphere and acids. This metal has contributed to the advance to civilization almost as much as copper and iron. Two general types of nickel ores are found, sulfide and oxide.

2. Source and Production

Production of all domestic nickel ore comes from a lateritic nickel silicate open pit mine at Nickel Mountain in Oregon. There was only one metal producer in 1968. Other nickel is produced as a by-product of copper refining. The ferronickel produced in 1968 had a market value of about $28 million.

3. Industrial Consumption

The 1968 total domestic availability of nickel amounted to about 478.4 million pounds, with a domestic industrial demand estimated at 374.1 million pounds, utilized as shown in Table A-1-15 (page A-1-63). Manufacturers of chemical and allied products and petroleum refiners are the major users of nickel. Others are: fabricated metal products, 18 percent; aircraft industry, 26 percent; transportation and electrical machinery, 22 percent; household appliances and machinery (nonelectrical), 17 percent; contractors, ship building and repair, and others, the remaining 12 percent.

4. Future Outlook

The projected annual growth rate for nickel demand, between 1968 and the year 2000, has been estimated at 2.8 and 4.0 percent. This converts into a volume figure of between 895 and 1,295 million pounds.

5. Waste Characteristics

The accumulation of solid wastes through 1968 in the nickel industry amounts to greater than 11.5 million tons of waste, covering an estimated 165 acres, and accumulating at a yearly rate of 1.2 million tons (Reference 10).

- Mine Waste — 1.8 million tons of crude ore are handled annually; sorting produces 300,000 tons of mine waste.

- Mill Tailings—There are 200,000 tons of mill tailing wastes generated annually, covering 25 acres of land surface.

- Slag—Since 1954, 10 million tons of nickel generated slag has been produced covering 125 acres of land surface. This is shown in Table A-1-19.

Table A-1-19
Estimated Magnitude of Solid Waste
Accumulations for Nickel

State and Type of Solid Waste	Accumulated thru 1968		1967	
	Tons (thousands)	Acres	Tons (thousands)	Acres
Oregon				
Mine waste				
Mill tailings	1,500	25	200	5
Smelter slag	10,000	125	1,000	10
Total	11,500	150	1,200	15

6. Associated Hazards

Nickel and its compounds are of concern as air pollutants because harmful effects of exposure to these materials have been observed among industrial workers. Exposure to airborne nickel dust and vapors may have produced cancers of the lung and sinus, other disorders of the respiratory system, and dermatitis. There is substantially higher mortality rate among nickel workers due to sinus cancer—up to 200 times the expected number of deaths. However, since other metal dusts have also been present in industrial exposures to nickel, it has not been possible to determine whether nickel is the carcinogen. Yet experiments have shown that nickel carbonyl and nickel dusts can induce cancer in animals. Nickel-contact dermatitis was found in 77 percent of the females and 10 percent of the males suspected of having allergenic reactions to metals. No information on the effects of nickel air pollution on commercial and domestic animals, plants, or materials was found in the literature.

The most likely sources of nickel in the air appear to be emissions from metallurgical plants using nickel, engines burning fuels containing nickel additives, and plating plants, as well as from the burning of coal and oil, and the incineration of nickel products. In 1964, urban air concentrations of nickel averaged 0.032 $\mu g/m^3$ and ranged up to a maximum of 0.690 $\mu g/m^3$ in East Chicago, Indiana.

Emission of nickel in particulate form can be controlled using normal control devices, such as precipitators, baghouses, and scrubbers. Nickel carbonyl, which is gaseous, must first be decomposed by heat before it is removed as a particulate.

No information has been found on the economic costs of nickel air pollution or on the costs of its abatement.

Methods of analysis are available which can be used to detect nickel at the 0.0064 $\mu g/m^3$ level and nickel carbonyl at the 7 $\mu g/m^3$ level.

Further studies are suggested in the following areas:

- Determination of the chemical composition of nickel compounds in the atmosphere. Measurement of the concentration of nickel near suspected sources, including metallurgical plants; vehicles' exhausts; and coal and oil-burning, plating, and incineration facilities. Measurement and analysis of the concentration of nickel in the emissions from these sources.

- Determination of the effect of nickel air pollution on plants and animals.

(7) SIC 109—Miscellaneous Metal Ores

The following metals are included in this section:

- Mercury
- Titanium
- Vanadium

Other metallic minerals:

- Antimony
- Arsenic
- Beryllium
- Cadmium
- Gallium
- Germanium
- Selenium
- Tellurium
- Thallium

1. Description

Mercury is the only metal that is liquid at ordinary temperatures. It is found in many minerals but is recovered almost entirely from the red sulfide mineral cinnabar.

2. Source and Production

Domestic output comes from a large number of small properties. They were 87 active mines in 1968; 53, which accounted for 74 percent of the total output, were in California. Nevada was second with 17 mines and 17 percent of total product, followed by Oregon with 6 mines and 3 percent. The remainder comes from 11 mines in Arizona, Alaska, Idaho, Texas, and Washington.

3. Industrial Consumption

The 1968 total domestic availability of mercury was 105,587 76 pound flasks, with the industrial demand being 75,422 flasks, utilized as shown in Table A-1-20. Largest consumers include the manufacturers of fungicides, dental preparations, electrical apparatus, paints, papers, pharmaceuticals, and other products.

4. Future Outlook

We projected annual growth for mercury demand in the years between 1968 and the year 2000 to be set at 1.5 and 2.8 percent, which converted into volume will range between 120,000 to 180,000 flasks in the year 2000.

Table A-1-20
Industrial Consumption Chart

SIC	SIC 109 Miscellaneous Metal Ores Description	Antimony (short tons)	Arsenic (short tons)	Beryllium (short tons)	Cadmium (1000 lb)	Gallium (Kgs)	Germanium (1000 lb)	Gold (Mil. Troy OZ's)	Indium (1000 Troy OZ's)	Mercury (76 lb Flasks)	Selenium (1000 lb)	Silver (Mil Troy OZ's)	Tellurium (1000 lb)	Thallium (lb)	Titanium (1000 short tons)	Vanadium (short tons)
28	Chem. & Allied Prod.												10			190
30	Rubber & Plastics	3600											24			
32	Stone, Clay & Glass	2300														
33	Primary Metal												182			
281	Industrial Chem.	3100														
322	Glass & Glassware		4100								300					
333	Nonferrous Alloys		700													
363	Household Appliance															
366	Communication Equip.															
367	Electronic Components															
372	Aircraft Parts				*800											1045*
373	Ship & Boat Build.															
1925	Guided Missiles			35												
2621	Paper Mills														75	
2812	Alkalies & Chlorine									17453						
2816	Inorganic Pigments	See (281)									150					
2818	Indust. Organic Chem.				1500*											
2819	Indust. Inorganic Chem.		900													
2821	Plastics & Resins				2500*					1914					44	
2833	Medical Chemicals		300							17526						
2851	Paints & Allied Chem.														243	
2879	Agricultural Pesticides		17900											600		
2893	Printing Ink									See (2833)					10	
2899	Misc. Chem. Products	3900														
3229	Glass and Glassware					7.0					See (322)					
3443	Fabricated Metal Prod.			35											10	
3471	Coating & Engraving				5900*											
3566	Pwr. Transmission	2200				26.5										
3573	Electronic Computing			40*										1000		
3579	Office Machines										250					
3585	Air Conditioning															

*Estimated

Table A-1-20
(Continued)

SIC	SIC 109 Miscellaneous Metal Ores Description	Antimony (short tons)	Arsenic (short tons)	Beryllium (short tons)	Cadmium (1000 lb)	Gallium (Kg's)	Germanium (1000 lb)	Gold (Mil. Troy Oz's)	Indium (1000 Troy Oz's)	Mercury (76 lb Flasks)	Selenium (1000 lb)	Silver (Mil. Troy Oz's)	Tellurium (1000 lb)	Thallium (lb)	Titanium (1000 short tons)	Vanadium (short tons)
3611	Elect. Meas. Instr.			45												
3612	Pwr. Distribution										250					
3613	Switch Gear Apparatus			90 *												
3623	Welding Apparatus		40*													
3627	Elec. & Nuclear Det.						8.0									
3629	Elec. Indust. Apparatus															
3641	Electric Lamps									See 3692						
3643	Current Carrying Wire								200							
3650	Consumer Elect.						37							4300		
3660	Communication Equip.															
3662	Radio T.V. Equip.		25*													
3674	Semiconductors					180 to 320					See 3612					
3679	Elect. Components							2.2								
3691	Storage Batteries	21000														
3692	Primary Batteries				400*					19686		5.8				
3714	Motor Vehicles Parts				1300*											
3729	Aircraft Parts														7	
3772	Aircraft Engines														8	
3821	Mech. Meas. Equip					12 to 48				7867						
3843	Dental Equip.							0.8								
3861	Photographic Equip.											41.6				
3911	Jewelry Prec. Metals							4.7				4.5				
3914	Jewelry & Silverware											43.6				
3996	Linoleum, Asphault														12	
7391	Commercial R&D Labs								150							
	Industrial Stock	6,626*	2,300	256	1,069	100	-	13.4	400	22,466	428	320.9	157	25,200	518	3,805
	Export & Others	7,901	-	111	1,458*	8 to 32	0.5	24.3	50	18,575	604	170.8	5	600	75	667
	Total	51,527	23,900	677	14,927	300 to 500	79	45.5	950	105,487	1,982	628.8	378	31,700	1,002	10,177

*Estimated

5. Waste Characteristics

Mine wastes generated, to date, by the mercury industry exceeds 6.8 million tons. Most mine dumps are small, averaging less than 150,000 tons. Volume of mill tailings and retort furnace rejects presently amounts to more than 19.3 million tons, and will increase to approximately 1.6 million tons annually. All mercury wastes, to date, cover about 640 acres of land in sparsely populated areas (Reference 10) as shown in Table A-1-21.

TITANIUM

1. Description

Titanium is a low-density, silver-white metal and its importance lies in its lightness, strength, and resistance to corrosion. Titanium alloys possess the tensile strength and hardness approaching that of many steel alloys; they have good impact strength and fatigue resistance.

Table A-1-21
Estimated Magnitude of Solid Waste Accumulations for Mercury

State and Type of Solid Waste	Accumulated thru 1968		1967	
	Tons (thousands)	Acres	Tons (thousands)	Acres
Arizona				
Mine waste and	60	30	Insignificant	
Mill tailings				
Smelter slag				
Total	60	30		
California				
Mine waste	6,000			
Mill tailings	15,000		1,000	10
Smelter slag				
Total	21,000	420	1,000	10
Idaho				
Mine waste and	300	10	15	3
Mill tailings				
Smelter slag				
Total	300	10	15	3
Nevada				
Mine waste	300			
Mill tailings	1,400		500	5
Smelter slag				
Total	1,700	50	500	5
Oregon				
Mine waste and	150	35		
Mill tailings*	1,000	75	100	5
Smelter slag				
Total	1,150	110	100	5

* Furnace rejects

2. Source and Production

Approximately one million tons of titanium concentrates are produced yearly from mines in New Jersey, New York, and Virginia. In 1968, the U. S. received 15 percent of its ilmenite from Canada, its entire rutile supply from Australia and Sierra Leone, and 25 percent of titanium metal from the United Kingdom. The U. S. accounted for half of the world's total, and consumes about two-thirds that amount.

3. Industrial Consumption

The 1968 total domestic availability of titanium was 1,002 thousand short tons, with an industrial demand of 458 thousand short tons, utilized as shown in Table A-1-20 (page A-1-87). Major users include: paints and allied products, paper, plastics, floor coverings, aircraft, fabricated plate work, and others.

4. Future Outlook

The projected annual growth rate for titanium demand between 1968 and the year 2000 has been set between 4.1 and 6.5 percent. These rates imply volume values between one and 2.4 million tons of metal in the year 2000.

5. Waste Characteristics

Mine wastes, Essex County, New York, totals over 53 million tons covering 275 acres; milling wastes add an additional 5 million tons covering 55 acres. In Virginia, combined mill and mine waste contain 6.2 million cubic yards, covering 87 acres. Present production methods will generate six million tons annually (Table A-1-22).

Table A-1-22
Estimated Magnitude of Solid Waste
Accumulations for Titanium

State and Type of Solid Waste	Accumulated thru 1968		1967	
	Tons (thousands)	Acres	Tons (thousands)	Acres
New York				
Mine waste and	58,000	275	5,000	8
Mill tailings	5,000	55		
Smelter slag				
Total	63,000	330	5,000	8
Virginia				
Mine waste	11,160	87	900	10
Mill tailings				
Smelter slag				
Total	11,160	87	900	10

VANADIUM

1. Description

Vanadium, a relatively abundant element in the earth's crust, is recovered principally as a co-product of other metals. It is chiefly used as an alloying element for nuclear applications, and as a catalyst.

2. Source and Production

Vanadium oxide is recovered in the U.S. from ores of domestic or foreign origin by three companies at four plants. One other company produces a vanadium ferroalloy principally from imported slag. The U.S. is the principal producer as well as the principal user of the metal.

3. Industrial Consumption

In 1968, the total domestic availability of vanadium was 10,177 short tons, with a domestic demand of 5,770 short tons, utilized as shown in Table A-1-20 (page A-1-87). Construction products are the principal consumers, followed by transportation, construction machinery, metal machinery, and chemical products.

4. Future Outlook

The projected annual growth rate for vanadium demand has been set at between 4.8 and 6.0 percent during the period of 1968 to 2000. This rate converts to a volume range of between 23,500 to 37,500 tons in the year 2000.

5. Waste Characteristics

The solid wastes associated with the production of vanadium are insignificant.

6. Associated Hazards

Vanadium is toxic to humans and animals; through inhalation of relatively low concentration (less than 1,000 $\mu g/m^3$), it has been found to result in inhibition of the synthesis of cholesterol and other liquids, cysteine, and other amino acids, and hemoglobin. Low concentrations also act as strong catalysts on serotinin and adrenaline.

Chronic exposure to environmental air concentrations of vanadium has been statistically associated with incidences of cardiovascular diseases and certain cancers.

Human exposure to high concentrations of vanadium (greater than 1,000 $\mu g/m^3$) results in a variety of clinically observable adverse effects whose severity increases with increasing concentrations. These effects include irritation of the gastrointestinal and respiratory tracts, anorexia, coughing (from slight to paroxysmal), hemoptysis, destruction of epithelium in the lungs and kidneys, pneumonia, bronchitis and bronochopneumonia, tuberculosis, and effects on the nervous system ranging from melancholia to hysteria.

No information has been found on adverse effects of atmospheric vanadium concentrations on vegetation or on commercial or domestic animals.

What is known about the effects of vanadium on materials related mostly to the corrosive action of vanadium, acting (together with sulfur dioxide) on oil- and coal-fired boilers, especially those using vanadium-rich residual oils and coals.

The major sources of vanadium emissions are the metallurgical processes producing vanadium metal and concentrates; the alloy industry; the chemical industry; power plants and utilities using vanadium-rich residual oils; and, to a lesser extent, the coal and oil refining industries. Vanadium production is concentrated in the states of Colorado, Utah, Idaho, and New Mexico, while the highest concentration of industries producing vanadium chemicals is found in New Jersey and New York. Domestic vanadium consumption has more than doubled since 1960, and the domestic mine production of ores and concentrates increased from 1,482 short tons of vanadium in 1945 to 5,226 short tons in 1965.

In communities in the U.S. in which vanadium concentrations were measured, the average values (quarterly composites) ranged from below detection (0.003 $\mu g/m^3$) to 0.30$\mu g/m^3$ (1964), 0.39$\mu g/m^3$ (1966), and 0.90$\mu g/m^3$ (1967).

Little information is available on the economic losses due to vanadium air pollution or on the costs of abatement. One report indicated that measures taken to reduce the loss of vanadium to the atmosphere from an oil-fired steam generator resulted in recovery of commercially valuable vanadium pentoxide, thereby producing a profit from air pollution abatement. No other information was noted in the literature on control procedures specifically intended to reduce used air pollution caused by vanadium. However, customary methods used to control particulate emissions in general are considered suitable to the industrial processes using vanadium or vanadium-containing fuels.

Methods of quantitative analysis of vanadium in the environmental air include colorimetry, atomic absorption spectroscopy, emission spectrography, and recently polarography. The trend is toward more use of spectrographic and spectrophotometric methods, some of which are more sensitive than the other methods and easily automated. Sensitivities on the order of 0.001 $\mu g/m^3$ are reported.

Further study is suggested in the following areas:

- Determination of the relationships of low concentrations of vanadium in various oxidation states with enzyme inhibition, cardiovascular disease, and cancer.
- Determination of the concentration and valence of vanadium near oil and coal burning industries (especially those burning vanadium-rich oil), and the vanadium metallurgical and chemical industries.
- Evaluation of the abatement and economics of vanadium air pollution control.

ANTIMONY

1. Description

Antimony, one of the oldest metals continuously used by man, is a silvery-white, brittle, crystalline solid which exhibits poor electrical and heat conductivity. It is chiefly obtained as a by-product or co-product of base metal ores, and finds industrial use in batteries and in metal alloys. It is also used in fire-retardant chemicals, glass, rubber, plastic, enamels, and small arms ammunition.

2. Source and Production

The current domestic production of antimony comes as by-product cathode metal from silver ores mined in the Cour'd Alene District of Idaho from three mines. Over 80 percent of the antimony metal derived from domestic and imported ores was produced at a single smelter in Texas, with a small plant in Idaho contributing the remainder from locally produced concentrates. Antimony metal and oxide producers are essentially large, vertically integrated companies.

3. Industrial Consumption

The 1968 total U. S. availability of antimony amounted to 51, 527 short tons, with an annual industrial demand of 44, 792 short tons, utilized as shown in Table A-1-20. (page A-1-87). The principal users of domestic antimony include: storage batteries, 47 percent of total; fire retardant chemicals, rubber, and plastics, 17 percent; industrial chemicals, stone, clay, and glass products, 12 percent; industrial machinery, 5 percent; communications and others, the remaining 19 percent.

4. Future Outlook

The projected annual growth rate of antimony demand between 1968 and the year 2000 has been estimated at an average of 2. 2 percent. This converts to a volume figure of between 63, 000 and 115, 000 tons in the year 2000.

5. Waste Characteristics

The accumulated mine wastes and mill tailings attributed to the antimony industry up to the present is approximately 500, 000 tons, covering a 20-acre land area (Table A-1-23).

Table A-1-23
Estimated Magnitude of Solid Waste Accumulations for Antimony

State and Type of Solid Waste	Accumulated thru 1968	
	Tons (thousands)	Acres
Idaho		
Mine waste and	500	20
Mill tailings		
Smelter slag		
Total	500	20

ARSENIC

1. Description

Arsenic is a steel gray, brittle crystalline, semi-metallic solid which tarnishes in air, and oxidizes rapidly when heated. The metal is a minor constituent of copper, gold, and silver. It is extracted from other ores as a fume or by skimming.

2. Source and Production

Arsenic is produced as a by-product of base-metal ores. Arsenic smelter segregated from other copper smelters supplements that recovered at Tacoma. Currently, U. S. smelter production is about one-fourth of the domestic supply; the remainder is imported. The world supply of arsenic exceeds the current demand, with other materials being used to a greater degree for pesticide markets.

3. Industrial Consumption

In 1968 the total domestic availability of arsenic amounted to 26, 200 short tons, with an industrial demand of 23,900 short tons utilized as shown in Table A-1-20 (page A-1-87). The agricultural chemicals (pesticides) industry is by far the greatest user of arsenic (75 percent), followed by the glass, organic chemicals, nonferrous alloys, and medical chemical industries.

4. Future Outlook

The projected annual growth rate for arsenic demand in the period of 1968 to 2000 has been set at between 0.8 and 2.3 percent which, when converted to volume, amounts to between 31,000 to 32,000 tons in the year 2000.

5. Waste Characteristics

The solid wastes derived from arsenic are considered to be insignificant, since it is totally derived from other base metal ores.

6. Associated Hazards

Arsenic is toxic, to some degree, in most chemical forms. Arsenical compounds may be ingested, inhaled, or absorbed through the skin. Industrial exposure to arsenic has shown that it can produce dermatitis, mild bronchitis, and other upper respiratory tract irritations including perforation of the nasal septum. However, because of the irritant qualities of arsenic, it is doubtful that one could inhale sufficient amounts to produce systemic poisoning.

Skin cancer can result from prolonged therapeutic administration of arsenic. Similar cancers have not been observed among industrial workers. Moreover, lung tumors which resulted from inhaling mixed industrial dusts were often thought to be the result of inhaling arsenic. Recently, this relationship has been questioned because animal experiments have failed to demonstrate that arsenic is a carcinogen. Therefore, the causal relationship between cancer and arsenic is disputed.

Arsenic is poisonous to both animals and plants, but no damage to materials was found.

Two air pollution episodes in the U. S. have shown that there is an arsenical air pollution potential at every smelter which refines arsenical ores.

Arsenical compounds are used as insecticides and herbicides. Although the use of arsenical pesticides declined sharply after the appearance of DDT and 2,4-D, arsenical compounds are still used as desiccants, herbicides and sterilants. Some undetermined amounts of air pollution take place during spraying and dusting operations with arsenical pesticides. Pollution from cotton gins and cotton trash burning has been cited as an important source of agricultural pollution. While the emission rates from cotton trash burning have not been determined, as much as 1,258,000 $\mu g/m^3$ of exhaust air (580,000 $\mu g/min$) may be emitted during the ginning operation. This produced concentrations of only 0.14 $\mu g/m^3$ of arsenic in the air 150 feet from the gin.

Arsenic is found to the extent of approximately 5$\mu g/m^3$ in coal. Therefore, the air of cities which burn coal contains some arsenic. Air quality data from 133 sites monitored by the National Air Sampling Network showed an average daily aresenic concentration of 0.02 $\mu g/m^3$ in 1964.

Control of arsenic emissions requires special attention to the temperature of exhaust gases since arsenic trioxide sublimes at 192°C. For this reason exhaust fumes must be cooled to approximately 100°C prior to removing them as particulates.

No information has been found on the economic costs of arsenic pollution or on the costs of its abatement.

Analytical methods are available to determine aresenic at the concentration found in ambient air.

Further studies are suggested in the following areas:

- Determination of the carcinogenic effect of long-term exposure to low concentrations of arsenic in the atmosphere.
- Measurement of the concentration of arsenic near smelters, pesticide dusting and spraying operations, cotton gins, and places where cotton trash is burned.

BERYLLIUM

1. Description

Beryllium metal has a high melting point and is exceptionally strong, rigid and very light. Beryllium and its compounds have certain unique properties which, regardless of cost, promise a growing application in special uses. The commercial source of beryllium is beryl, which is hand-sorted from certain pegmatites.

2. Source and Production

The production of hand-sorted beryl in the United States is negligible, and requirements are met almost entirely from foreign imports. South Dakota is the nation's principal producer of beryl, followed by Colorado and New Mexico. All domestic ores are mined from small open pit, and underground mines.

3. Industrial Consumption

The 1968 total domestic availability of beryllium was 667 short tons, with a domestic industrial demand of 384 short tons, utilized as shown in Table A-1-20 (page A-1-87).

4. Future Outlook

The projected growth rate for beryllium demand, between 1968 and the year 2000, indicates a volume demand in the year 2000 of between 1,930 and 1,660 short tons.

5. Waste Characteristics

An accumulation of mine waste for this industry, to date, amounts to 750,000 tons, covering an area of 2,000 acres. All of this acreage is in South Dakota. Tonnage and surface area of mill tailing wastes in other states is insignificant (Reference 10).

6. Associated Hazards

Inhalation of beryllium or its compounds is highly toxic to humans and animals, producing body-wide systemic disease commonly known as beryllium disease. Both acute and chronic manifestations of the disease are known. The effects of beryllium intoxication can be mild, moderate, or severe, and can prove fatal, depending on the duration and intensity of exposure.

Acute beryllium disease is manifested by a chemical penumonitis ranging from transient pharyngitis or tracheobronchitis to severe pulmonary reaction. As of June 1966, 215 acute cases had been recorded in the Beryllium Case Registry.

Chronic beryllium disease generally occurs as lesions in the lung, producing serious respiratory damage and even death. However, every organ system may be involved in response to beryllium exposure, except for the organs in the pelvic area. The chronic form is characterized by a delay in onset of disease, which may occur weeks or even years after exposure. In June 1966, 498 chronic cases had been recorded, plus 47 acute-to-chronic cases.

Of the total 760 cases recorded in the Beryllium Case Registry, 210 fatalities, or 27.5 percent, had occurred by June 1966.

Cancer has been produced experimentally in animals, and 20 cases of cancer have been found (as of 1966) in humans afflicted with beryllium disease. However, insufficient information exists at this time to causally relate beryllium poisoning to development of cancer in humans.

Beryllium and its compounds can produce dermatitis, conjunctivities, and other contact effects; however, these manifestations are rare.

There is some evidence that beryllium in soil is toxic to plant life; no evidence was found on the effects of atmospheric beryllium on plants or on materials.

The major potential sources of beryllium in the atmosphere are industrial. The processes of extraction, refining, machining, and alloying of the metal produce toxic quantities of beryllium, beryllium oxide, and beryllium chloride, which if allowed to escape into the atmosphere would cause serious contamination. Recognition of the serious hazards to health from these sources has led to adaptation of control procedures minimizing this potential. However, beryllium in limited quantity is emitted from these industrial processes, and danger also exists from accidental discharges. One major source of beryllium contamination—the use of beryllium in fluorescent light tubes—was discontinued in 1949. Other sources could be the use of metallic beryllium in rocket fuels, and the combustion of coals. Rocket fuels could present a hazard in the handling and storage of the powdered metallic beryllium used as an additive in the fuels. Also, the exhaust fumes, which contain oxidized beryllium as well as other compounds of beryllium, would be of significance in local soil and air pollution if not contained. As beryllium is a normal constituent (above 2 ppm) of coals, the combustion of coal may add a significant quantity of beryllium to the atmosphere.

Measurements are made of the beryllium concentration at 100 stations in the U.S. The average 24-hour concentration is less than 0.0005 $\mu g/m^3$; the maximum value recorded during the 1964-1965 period was 0.008 $\mu g/m^3$.

Abatement measures have been implemented industry-wide, with a very high degree of success. Conventional air-cleaning procedures have been employed, including the use of electrostatic precipitators, baghouses, scrubbers, etc. These procedures have enabled the beryllium industry to meet the industrial hygiene standards established for beryllium.

Data on the economic losses resulting from beryllium air pollution are not available. Court cases are pending in the State of Pennsylvania, however, which may provide data on the economic values of impairment to health resulting from exposure to beryllium. Only one analysis of the costs for abatement was found. This study indicated that the added costs for control amounted, in 1952, to approximately 20 percent of the normal cost of operation for the particular plant analyzed.

Methods of analyzing beryllium in the atmosphere are available, and are adequate for normal industrial processes. The most common methods are the Zenia method. The Zenia method is relatively simple, works well with high concentrations, and provides sensitivity on the order of 0.5 $\mu g/m^3$. It can also be used subjectively to provide a quick spot-check for the presence of beryllium materials. The morin fluorescent method provides a higher sensitivity range (0.01 $\mu g/m^3$) and is suitable for monitoring out-of-plant concentrations in the vicinity of beryllium processing plants if a large enough volume of air is sampled. The spectrographic process gives even higher sensitivities (0.003 $\mu g/m^3$) and is suitable for monitoring concentrations in the general atmosphere.

However, none of the currently available procedures provides for discrimination between the various compounds of beryllium, or differentiation between the "low-fired" (highly-toxic) and the "high-fired" (less toxic) forms of beryllium oxide.

Further studies are suggested in the following areas:

- Further research into the pathogenesis of beryllium disease, with particular emphasis upon the effects of protracted exposure to low concentrations.
- Further research into the carcinogenicity of beryllium compounds.
- Analysis of the contribution of coal combustion to beryllium pollution of the atmosphere.
- Development of procedures for analysis of different compounds of beryllium present in the atmosphere.
- Development of improved methods for characterization of combustion products of rocket fuels containing beryllium compounds.

CADMIUM

1. Description

Cadmium is a relatively rare metal whose major value is its ability to protect more common materials.

It is a soft malleable, silver-white metal when freshly cut, and dulls due to formation of oxides on exposure to air.

2. Source and Production

The U. S. cadmium-producing industry comprises nine firms that produce cadmium metal as an integral part of their zinc operations. In addition, two other plants not integral to zinc plants produce cadmium from residues, flue dust, or scrap material.

3. Industrial Consumption

In 1968 the total domestic availability of cadmium was about 14, 927 thousand pounds, with a demand of 13, 328 thousand pounds utilized as shown in Table A-1-20 (page A-1-87). Cadmium is used in transportation, aircraft and boats, electroplating, batteris, pigments, plastics, etc.

4. Future Outlook

The projected annual growth rate for the cadmium demand for the period 1968 to 2000 has been set at from 1. 4 to 3. 5 percent which, translated into volume, is from 12. 2 to 39 million pounds by the year 2000.

5. Waste Characteristics

Solid wastes are essentially considered in the zinc area. Fumes from cadmium are extremely toxic. Fumes of zinc smelters are collected so there is not too much cadmium in the air.

6. Associated Hazards

Cadmium and cadmium compounds are toxic substances by all means of administration, producing acute or chronic symptoms varying in intensity from irritations to extensive disturbances resulting in death. However, despite increasing use of this metal and increasing attention to its toxic nature, the exact manner in which it affects human or animal organisms is not yet known. Cadmium is toxic to practically all systems and functions of the body, and is absorbed without regard to the levels of cadmium already present, thereby indicating the lack of a natural homostatic mechanism for the control of organic concentrations of cadmium.

Inhalation of cadmium fumes, oxides, and salts often produces emphysema, which may be followed by bronchitis. Prolonged exposures to airborne cadmium frequently cause kidney damage resulting in proteinuria. Cadmium also affects the heart and liver. Statistical studies of people living in 28 U.S. cities have shown a positive correlation between heart diseases and the concentration of cadmium in the urban air. Cadmium may also be a carcinogen. While there is little evidence to support this conclusion from studies of industrial workers, animal experiments have shown cadmium may be carcinogenic. No data were found that indicated deleterious effects produced by airborne cadmium on commercial or domestic animals. However, experiments with laboratory animals have shown that cadmium affects the kidneys, lungs, heart, liver, and gastro-intestional organs, and the nervous and reproductive systems. No data were found on the effects of cadmium air pollution on plants or materials.

The metals industry is the major source of emissions of cadmium into the atmosphere. Cadmium dusts and fumes are produced in the extraction, refining, and processing of metallic cadmium. Since cadmium is generally produced as a by-product in the refining of other metals, such as zinc, lead, and copper, plants refining these materials are sources of cadmium emissions as well as of the basic metal. Also, because cadmium is present in small quantities in the ores of these metals, cadmium emissions may occur inadvertently in the refining of the basic metal.

Common sources of cadmium air pollution occur during the use of cadmium. Electroplating, alloying, and use of cadmium in pigments can produce local contaminations of the atmosphere. Also, since cadmium is added to pesticides and fertilizers, the use of these materials can cause local air pollution.

In 1964, the average concentration of cadmium in the ambient air was 0.002 $\mu g/m^3$, and the maximum concentration was 0.350 $\mu g/m^3$.

Air pollution control procedures are employed at some metal refinery plants in order to recover the valuable cadmium that would otherwise escape into the atmosphere. Electrostatic precipitators, baghouses, and cyclones are effectively used for abatement. However, little information has been found on the specific application of these procedures for the purpose of controlling cadmium air pollution. The procedures for recovering cadmium from exhaust in a copper extraction plant collected significant quantities of valuable cadmium, at the same time reducing local air pollution levels.

No information has been found on the economic costs of cadmium air pollution or on the costs of its abatement. Methods are available for the analysis of cadmium in the ambient air.

Further studies are suggested in the following areas:

- Research into the effects of cadmium on human, animal, and plant health
- Research into the carcinogenic effects of cadmium
- Quantitative analysis of the emissions of cadmium into the atmosphere from industrial sources.

GALLIUM

1. Description

Gallium is a by-product derived entirely from processing certain aluminum and zinc ores. It currently finds application in the electronics industry.

2. Source and Production

Two firms are producing gallium in the U.S.

3. Industrial Consumption

In 1968, the total domestic availability of gallium was estimated between 300 to 5000 kilograms, with a demand between 200 to 400 kilogram, utilized as shown in Table A-1-20 (page A-1-87). Principal users are the electronic industry, and manufacturers of mechanical measuring devices.

4. Future Outlook

The projected demand for gallium for the year 2000 has been set between 230 and 1,150 kilograms.

5. Waste Characteristics

The solid waste problem due to gallium is essentially insignificant since it is derived from other base metal ores.

GERMANIUM

1. Description

Germanium is metallic-looking but displays metallic chracteristics only under special conditions. It is a semi-conductor ranging between metal and insulator, and is used chiefly in the electronics industry.

2. Source and Production

Germanium is a minor by-product of ores mined primarily for zinc. As a primary metal it is wholly due to domestic production. One domestic refinery produces the metal by refining residues of zinc. Three secondary refineries in Pennsylvania and New Jersey process new scrap from manufacturers of electronic parts.

3. Industrial Consumption

In 1968, the total domestic availability and industrial demand for germanium was 79 thousand pounds, utilized as shown in Table A-1-20 (page A-1-87). The largest user was electronics, with some metal being used in pressed and blown glass.

4. Future Outlook

The projected annual growth rate for germanium demand, in the period 1968 to 2000, has been set between 0.9 and 3.0 percent, which, when converted to volume, implies a demand between 97,000 and 195,000 pounds of the metal by the year 2000.

5. Waste Characteristics

Solid wastes are insignificant since the metal is obtained principally from zinc ores.

SELENIUM

1. Description

Selenium is distributed widely in nature. However, it is mostly derived from its association with copper, iron, lead, and other metals.

2. Source and Production

At present selenium is derived domestically as a by-product of electrolytic copper refining. Five plants located in New Jersey and Maryland accounted for all selenium production in 1968.

3. Industrial Consumption

In 1968, the total domestic availability of selenium was 1,986 thousand pounds, with a demand of 1,100 thousand pounds, utilized as shown in Table A-1-20 (page A-1-87). Major uses include: electrical power distribution, glass industry, duplicating machines, pigments, etc.

4. Future Outlook

The projected annual growth rate for selenium in the period 1968 to 2000 has been set between 0.3 and 2.3 percent which, when converted to volume, amounts to between 1.2 and 2.2 million pounds in the year 2000.

5. Waste Characteristics

Solid wastes due to selenium are insignificant, since it is derived entirely from other base metal ores.

6. Associated Hazards

Selenium compounds, particularly the water-soluble compounds, are toxic to humans and animals. In humans, mild inhalation of selenium dusts, fumes, or vapors irritate the membranes of the eyes, nose, throat, and respiratory tract, causing lacrimation, sneezing, nasal congestion, coughing, etc. Prolonged exposure through inhalation can cause marked pallor, coated tongue, gastrointestinal disorders, nervousness, and a garlicky odor of breath and sweat. In animals, subacute selenium poisoning produces pneumonia and degeneration of the liver and kidneys. Furthermore, experiments with rats indicate that selenium may cause cancer of the liver.

The biochemical effects of elemental selenium and its compounds on humans is not as yet thoroughly understood. The selenium deficiency diseases found in animal species, as well as some of the frank selenium poisoning, have not been observed in man. Similarly, the carcinogenic hazard of selenium and the antagonistic effect of arsenic for selenium seen in animals are yet to be shown in humans. These are important factors that need clarification to properly evaluate the role of selenium and its compounds in air pollution.

There is no information indicating that amospheric selenium has any detrimental effect on plants or materials. Some plants contain large amounts of selenium that can be toxic to the plants themselves, as well as to humans and animals who ingest the plants.

Samples of snow, rain, and air taken in Boston, Mass., (1964-1965) show that the selenium content of the air is averaging 0.001 $\mu g/m^3$. Based on the selenium-to-sulfur ratio in these samples, the atmospheric selenium was probably from terrestrial sources, including the fuels and ores used by industry. Another source may be the burning of trash containing paper products. Some papers when analyzed contain as much as 6 ppm selenium. Selenium in paper may come from accumulation by the original tree or plant, or possibly from the manufacturing of the paper (from the use of pyrites in the process). Any vegetation which is burned may be a possible source of atmospheric selenium. Another source could be the refining of sulfide ores, particularly copper and lead ores.

Emissions of selenium and its compounds can be effectively controlled by use of electrostatic precipitators and water scrubbers.

No information has been found on the economic costs of selenium air pollution, or on the costs of its abatement. Methods of analysis are available that can measure quantitatively in the parts per billion or submicrogram region. However, none of the methods is simple, rapid, or applicable to continuous monitoring, and many of the methods are not specific for selenium. A rough estimate as to the magnitude of selenium in the atmosphere might be made from the concentration of sulfur in the atmosphere. This method would be valid if the sources of these two pollutants are sulfide ores, fossil fuels, or igneous and sedimentary rocks, since in these materials the average weight ratio of selenium to sulfur is 1×10^{-4}.

Further studies are suggested in the following areas:

- Further determination of the atmospheric concentration of selenium coupounds in the cities of the United States, particularly near copper refiners and other sulfide ore refiners, and near trash-burning sites.
- Determination of the long-term exposure effects on humans and animals, particularly in the concentration range found in the atmosphere.
- Determination of the amount of selenium in particulates.
- Investigation of the possibility of antagonistic, synergistic, or catalytic effect of selenium or its compounds with other substances in the environmental air.

TELLURIUM

1. Description

Tellurium is one of the rarest of elements, ranking 75th in order of abundance in the earth's crust. It rarely occurs in the native state and is usually assoicated with copper, lead, silver, gold, mercury, and bismuth ores.

2. Source and Production

Tellurium is a minor by-product of electrolytic refining of copper and lead, and producers of these commodities are producers of tellurium. Some of the tellurium producers in the United States are located in Carteret, N. J.; Baltimore, Md.; Perth Amboy, N. J.; Boyertown, Pa.; East Chicago, Md.; and Meapeth, N. Y. The U. S. is the world's leading tellurium producer and consumer.

3. Industrial Consumption

In 1968, the total domestic availability of tellurium was 378 thousand pounds, with a domestic demand of 221 thousand pounds, utilized as shown in Table A-1-20 (page A-1-87). Its greatest use is in the primary metals, rubber and plastics, and chemical industries.

4. Future Outlook

The projected annual growth rate for tellurium demand, during the period 1968 to 2000, has been set between 0.3 and 2.4 percent which, converted to volume, reaches between 240,000 and 485,000 pounds in the year 2000.

5. Waste Characteristics

Since tellurium is totally derived from other ores, there are no solid waste figures associated with the metal.

THALLIUM

1. Description

Thallium, a rare metal is recovered entirely as a by-product of processing certain base-metal ores, notably zinc. It is very malleable and softer than lead.

2. Source and Production

Thallium is produced domestically by a large nonferrous metal producing firm, The American Smelting and Refining Company, which maintains thallium-producing facilities along with its zinc operation.

3. Industrial Consumption

In 1968 the total domestic availability of thallium was 31,700 pounds, with a domestic demand of 6,500 pounds, utilized as shown in Table A-1-20 (page A-1-87). Chief consumers of thallium are the electronics industry and agricultural pesticides.

4. Future Outlook

The projected annual growth rate for thallium demand has been set at 1.6 percent for the period 1968 to 2000; the volume is expected to range between 6,000 and 9,500 pounds.

5. Waste Characteristics

Solid waste from thallium production is insignificant, since it is derived as a by-product from other base metal ores.

6. Associated Hazards

Thallium is highly toxic; once ingested it is not quickly eliminated from the body, and is cumulative. An antidote for thallium poisoning is not known.

SIC 11—ANTHRACITE MINING

1. Description

Fossil fuels presently account for, and will continue to account for, the bulk of our energy supply into the year 2000. These fuels include coal, petroleum and natural gas, and provide 96 percent of the nation's gross energy input. The remaining 4 percent is accounted for by hydropower and nuclear plants. Coal mining includes extraction of anthracite, bituminous, and lignite.

2. Source and Production

The anthracite industry, located primarily in Pennsylvania, is comprised of 246 underground mines, 130 strip pits, 127 culm and silt banks, 7 dredges, and 137 preparation plants (including primary screening stations) in 13 counties in northeastern Pennsylvania. The coal beds underlie a surface of 484 square miles, and are separated by geologic conditions into four distinct fields. The producing area is divided into three regions.

Organizationally, the industry ranges from small independent underground mines with as few as two employees, to large companies with multiple mining operations, preparation plants, and surface shops. In 1967, 15 of the largest companies produced 64 percent of the total anthracite output.

3. Industrial Consumption

In 1968, the domestic availability of anthracite coal amounted to 11,591 thousand short tons, utilized as follows:

Consumer	SIC Code	Availability (Thousand Short Tons)
Household and commercial	65, 70, 88	4,759
Electric Utilities	4911	2,203
Industrial	20, 28, 32	1,872
Primary Metals	33	1,280
U.S. Armed Forces	9189	913
Export		518
Other	99	46

The principal uses of anthracite ore are as an energy fuel, and as a source of industrial carbon. As an energy source, the largest use is for space heating, being specially sized for hand-fired furnaces to large automatic equipment. It is also heavily used for electric power generation. In the iron and steel industry, it is used in the manufacture of coke, sintering, and in place of coke in foundry processes. Other uses include the manufacture of briquets, burning cement and lime, in brick and ceramic kilns, curing agricultural products, and other applications where the use for a clean steady heat source is necessary. The railroad as a customer for anthracite has almost dissappeared.

Anthracite provides a carbon source for use in a variety of products, including the manufacture of telephone, water and chemical filtering and purification material, electrical and electronic equipment, and in the area of carbide products.

4. Future Outlook

The demand for anthracite in the U.S. is on the decline. In 1968,this demand approximated 10.2 million short tons, and is expected to decrease to between 1.0 to 3.6 million short tons. The most severed decline will be in the area of space heating, the industries major market. Since 1949, this decline was at an average annual rate of 8.9 percent but is expected to stabilize at about 40 percent of present demand. Decreases in the primary metal industries are attributed to (1) conversion to natural gas, (2) substitutions of plastics for some metals, and (3) increases in electric furnaces requiring less coke. An increase could be in the need for foundry coke. The future cost of mined coal will influence its use. Electricity-generation using anthracite is beginning to stabilize. The future increase in electric power demand (about 8.5 percent) annually) to the year 2000 may result in increased demand for anthracite near coal-producing regions.

5. Waste Characteristics

Waste characteristics for anthracite mining are included with those for bituminous coal and lignite mining in the following section.

SIC 12—BITNUMINOUS COAL AND LIGNITE MINING

1. Source and Production

The bituminous coal and lignite industry is widely dispersed throughout the nation. There are currently 5,300 active mines in the industry, controlled by 3,800 companies, with the majority of these, small operation. However, consolidation of smaller operations is the industry trend. Six leading coal producing states account for 86 percent of total domestic production, and 14 percent of the mines are responsible for almost 80 percent of the total output.

The bituminous industry requires that 73 percent of total output be transported chiefly by rail; hence, railroad rates influence the cost of coal and will affect the future of the industry.

2. Industrial Consumption

In 1968, the domestic availability of bituminous coal and lignite amounted to 637,858 thousand short tons, utilized as follows:

Consumer	SIC Code	Availability (thousand short tons)
Household and Commercial	651, 70, 88	15,224
Electric Utilities	49	294,739
Food and kindored Products	20	8,480
Paper and Allied Products	26	14,888
Primary Metal Industries	33	99,313
Stone, Clay and Concrete Products	32	13,003
Transportation	40, 44	417
Other Mineral and Manufacture	39	31,283
Chemical and Allied Products	28	21,483
Industry Stocks (as of 12/31/68)		87,462
Exports		50,637
Losses		929

The principal use of bituminous coal and lignite is almost exclusively that of a source of heat and power, with the major exception being in the production of metallurgical coke. The largest and most rapid growing market is the electric utility industry, accounting for 59 percent of total bituminous and lignite consumption in 1968. The next major area of importance is the primary metal industry for production of coke used in blast furnaces, and power for steel and rolling mills. This accounted for approximately 20 percent of 1968 consumption.

Declines in the use of bituminous coal and lignite in the past 20 years have occurred in the household and commercial market, and in the food and allied products where there has been a trend toward other energy sources, including oil and natural gas. The stone, clay, and glass industries other than cement have been declining steadily, while the paper and allied products showed a slight turn upward. Railroads and shipping which,were a large market for this fuel source, have virtually disappeared.

3. Future Outlook

The demand for bituminous coal and lignite has been on the decline since the early 1940's; when consumption ranged around 120 million tons per year, as compared to 15 million tons in 1968. It is anticipated that direct consumption will continue downward, because of shifts to other energy sources (e. g. , electricity, oil, and natural gas). However, coal will be utilized more and more to produce electrical power, and an increase in the need for synthetic gas and liquid fuels will require the additional use of bituminous coal and lignite.

The demand for these fuels in the U.S., which approximated 499 million tons in 1968, is expected to range from 1,275 million to 2,639 million tons in the year 2000.

4. Waste Characteristics

The mining and preparation activities for the anthracite, bituminous, and lignite industries are widely distributed in the U.S. A total of 24 states, in 1967, produced 557 million tons of coal, 95 percent of which was mined east of the Mississippi River. In the 1960's, approximately 1,500 strip mines excavated on the average of 12.8 cubic yards of overburden per tons of coal.

Unlike other mineral waste, coal wastes from all sources are most often deposited in the same area. Coal waste piles vary in size due to differences in mine production, preparation, and in seams and mining conditions. Although in some ways different, these culm banks have one characteristic in common; that is, they contain combustibles and as such are susceptible to spontaneous combustion.

Anchracite waste materials produced in the coal production process are primarily limited to four anthracite fields in northeastern Pennsylvania. A 1966 in-depth survey (Reference 11) by the Bureau of Mines regarding that region's waste showed that there were 863 refuse banks distributed through the area containing almost 910 million tons of material, occupying a total of about 12,000 acres.

Bituminous and lignite wastes are generated during the cleaning, sorting, and sizing of coal. The amount of raw coal mechanically cleaned and the amount of rejected waste have steadily increased due to increased efficiency of coal cleaning and quality demands by the consumer (Figure A-1-1). It is expected that the percentage of mechanically cleaned coal will remain essentially cosntant, but the percentage of waste will increase at a gradual rate (Figure A-1-2).

In addition to overburden and coal wastes, the combustion of coal produces ash, adding to the disposal

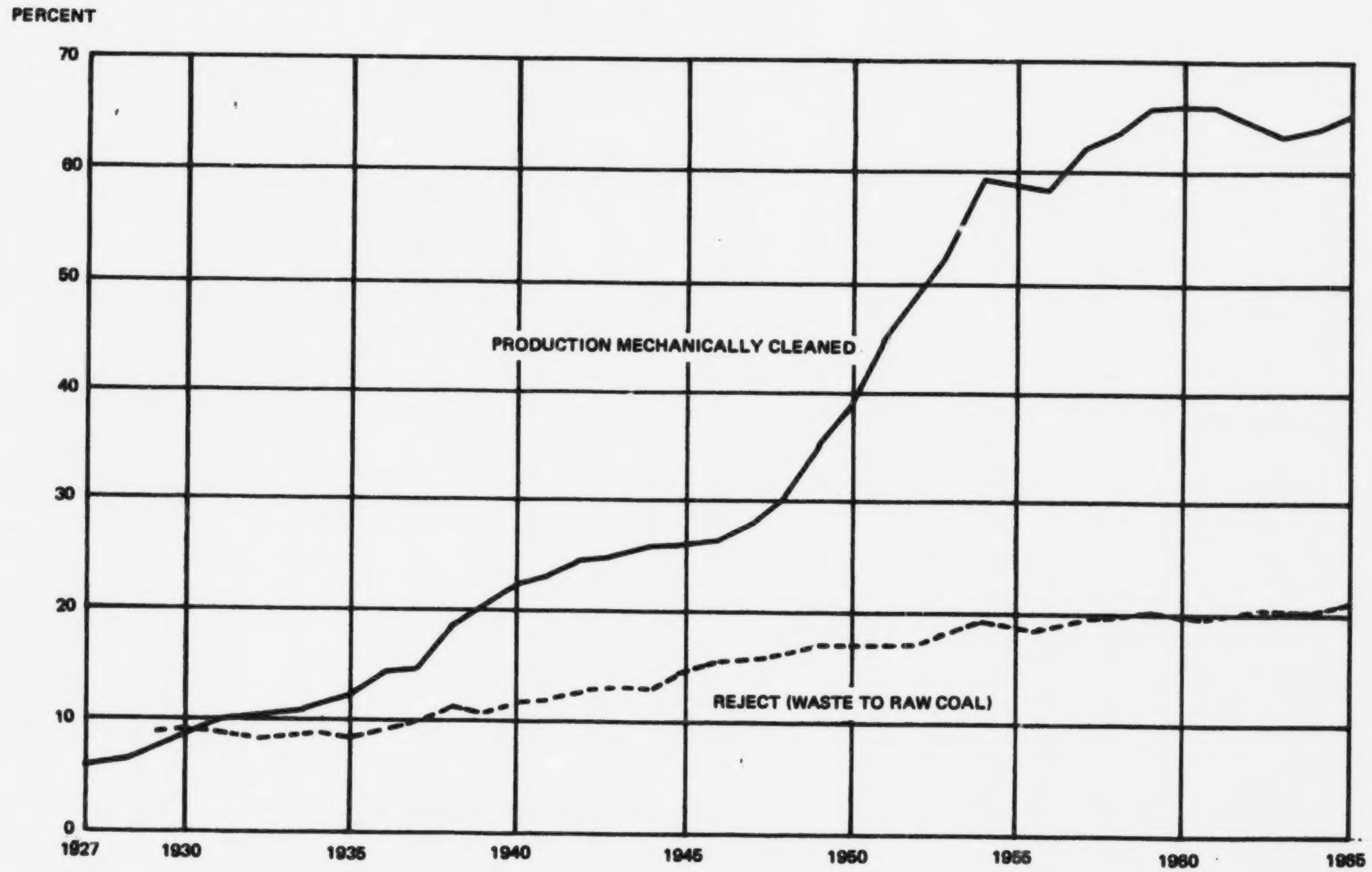

FIGURE A-1-1
Trends in the Portion of Total Production of Coal Which is Mechanically Cleaned and the Average Reject Percentage in the United States

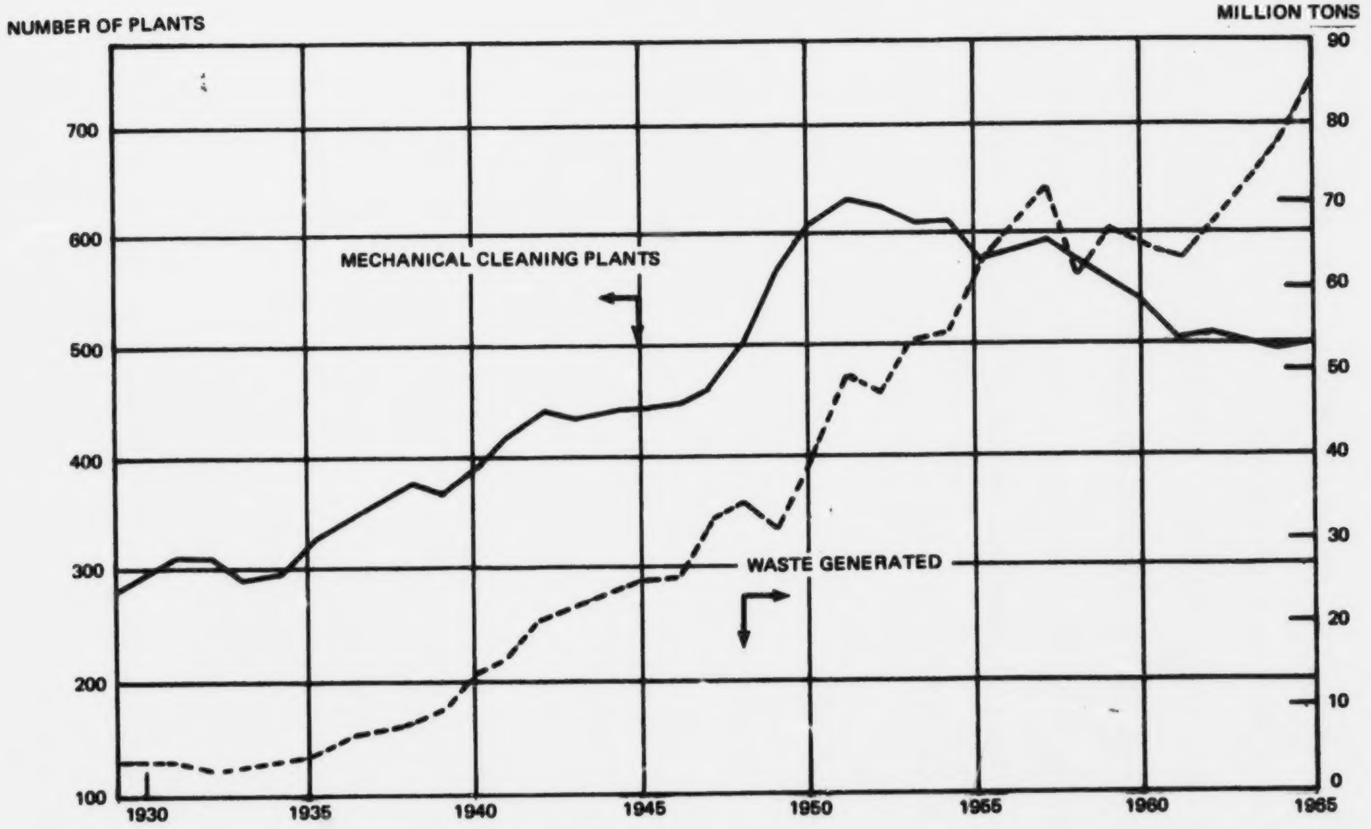

FIGURE A-1-2
Trends in the Amount of Waste Generated
at Mechanical Coal Cleaning Plants and the Number of Plants
in the United States

problem. The electrical power industry consumes vast amounts of coal and consequently produces more ash than any other consumer. The combustion process produces a volume of ash one-tenth the volume of coal consumed. Power companies pump this residual into settling ponds in slurry form. In 1965 electric companies were responsible for over 24,500,000 tons of ash. This residue is finding use as a concrete additive, road base stabilizer, and as agricultural soil conditioners.

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APPENDIX A-2

SIC 20—FOOD AND KINDRED PRODUCTS

The Food and Kindred Products industry (SIC code 20) provides the consumer with his daily sustenance as well as providing a market place for the rural farming community. Included in this industrial classification are: establishments which manufacture foods and beverages for human consumption; certain related products such as manufactured ice, chewing gum and vegetable and animal fats and oils; and prepared feeds for animals and fowl. In addition, establishments whose primary concern is the process and distribution of dairy products (e. g., milk and cream), and the extraction of animal vegetable oils, are included.

Since this report is designed to explore the production of wastes and utilization of waste disposal technology for each industry, the Food and Kindred Products industry appendix includes the following sections:

- Economic Statistics (including a description by SIC code classification)
- Waste Characteristics
- Disposal Practices

1. ECONOMIC STATISTICS

The Food and Kindred Products industry (SIC code 20) is a vital part of the economy. The scope of this industry encompasses most staple commodities from the field and/or manufacturer. This section covers the following general topics:

- SIC Code Classifications and Descriptions
- Number of Establishments and Locations
- Relative Concentration
- Major Raw Materials and Annual Production
- Employment Statistics
- Growth Patterns.

(1) SIC Code Classifications and Descriptions

The major SIC code 20 (Food and Kindred Products) includes nine general categories which are considered in this appendix. These categories (Reference 1), and a brief description of each, are as follows:

- 201 Meat Products—Includes establishments which slaughter livestock and other animals (except small game) to be sold or used in canning, curing, or the making of sausage, lard or other products on the premises. Establishments which use prepared carcasses and other materials to manufacture sausage or prepared meats and meat specialties by the curing, smoking, canning, and freezing of meats are also included, as well as establishments that kill, dress, package, and can poultry, rabbits, and other small game.

202 Dairy Products—Includes establishments which manufacture creamery butter, natural cheese, condensed and evaporated milk, ice cream and frozen desserts, and special dairy products such as processed cheese and malted milk. Establishments that process (pasteurize, homogenize, vitaminize and bottle) fluid milk and cream for wholesale or retail distribution are also in this category.

202 Canned and Preserved Fruits, Vegetables and Sea Foods—Includes establishments which can fruits and vegetables and their juices; manufacture catsup and similar tomato sauces, preserves, jams, and jellies, sun dry or artificially dehydrate fruits, vegetables and nuts, or manufacture packaged soup mixes from dehydrated ingredients; pickle and brine fruits, vegetables and manufacturing salad dressings, vegetable relishes, sauces and seasonings; and quick freeze and pack fruits, fruit juices, vegetables, and specialties. Also included are those establishments which cook and can fish and other sea foods; smoke, salt, dry or otherwise cure fish for trade; prepare fresh and raw or cooked frozen packaged seafood; and those which can specialty products such as health foods, baby food, and "nature" foods.

204 Grain Mill Products—Includes establishments which mill flour or meal from grain; manufacture prepared feeds for animals and fowls, including certain feed ingredients and adjuncts; manufacture cereal breakfast foods and related preparations; clean and polish rice, and manufacture rice flour and meal; and prepare blended flours and flour mixes. Establishments which mill corn or sorghum grain by the wet process and produce starch, syrup, oil, sugar and by-products such as gluten feed and meal, and manufacture starch from other vegetable sources are also included.

- 205 Bakery Products—Includes establishments which make bread, cakes and other perishable bakery products, as well as dry bakery products such as biscuits, crackers, and cookies.

- 206 Sugar—Includes establishments which manufacture raw sugar, syrup or finished cane sugar from sugar cane or sugar beets, as well as those which refine purchased raw cane sugar and sugar syrup.

- 207 Confectionary and Related Products—Includes establishments which manufacture candy including chocolate, salted nuts, other confections and related products, solid bars, and chewing gum. Establishments which shell, roast, and grind cocoa beans for making chocolate liquor are also included.

- 208 Beverages—Includes establishments which manufacture malt or malt by-products from barley or other grains, and all kinds of malt liquors; manufacture wines, brandy and brandy spirits (including bonded storerooms engaged in blending wines); manufacture alcoholic liquors by distillation and rectification, and cordials and alcoholic cocktails by blending processes or by mixing liquors and other ingredients; manufacture soft drinks and carbonated waters; and manufacture flavoring extracts, syrups, and fruit juices for soda fountains, soft drinks, and colors for bakers and confectioners.

- 209 Miscellaneous Food Preparations and Kindred Products—Includes establishments which manufacture cottonseed oil and by-product cake, meal, and linters; manufacture soybean oil and by-product cake and meal; manufacture animal oils including fish and other marine animal oils and by-product meal, and render inedible grease and tallow from animal fat, bones, and meat scraps; roast coffee, and manufacture coffee concentrates and extracts in powder, liquid, or frozen form; manufacture shortening, table oils, margarine and other edible fats and oils by further processing purchased animal and vegetable oils (no elsewhere classified). Establishments which manufacture ice for sale (including public utility operated companies); manufacture dry and canned macaroni, spaghetti and vermicelli noodles, and prepared foods and food specialities (not elsewhere classified) are also included.

(2) Number of Establishments and Locations

Since the Food and Kindred Products industry encompasses the whole United States, a general discussion of the overall industrial establishments is divided into four regions (Reference 2):

- Northeastern Region
- North Central Region
- Southern Region
- Western Region.

The major SIC code classifications are also discussed by region.

There were approximately 32,518 establishments in 1967, within the Food and Kindred Products industry. Although it appears that the major contributor was the North Central Region with 10,147 establishments, the diversification within the industry must be considered.

Table A-2-1
National and Regional Establishment Figures for the Food and Kindred Products Industry (1)

Total Establishments	Geographical Area
10,147	North Central Region
9,114	Southern Region
7,676	Northeastern Region
5,581	Western Region
32,518	United States

(1) 1967 data.

For example, in the Canned and Preserved Fruits, Vegetables, and Seafood classification, the Western Region contains more establishments than the other regions. The Southern Region was the main location for establishments in the sugar classification. Table A-2-2 gives the number of establishments in each region for nine industries.

(3) Major Raw Materials and Annual Production

Tables A-2-3 through A-2-10 provide information on the major raw materials and their 1967 annual production (Reference 2). Each table represents one of the major classifications within the Food and Kindred Products industry, and the products are shown within the applicable processing plant.

Table A-2-2

National and Regional Establishments for the Major Food Industries (1967).

SIC Code	Industry	Number of Establishments				
		Northeastern Region	North Central Region	Southern Region	Western Region	United States Region
201	Meat Products	901	1,633	1,623	757	4,914
202	Dairy Products	1,624	2,807	957	800	6,188
203	Canned and Preserved Fruits, Vegetables and Seafoods	758	746	977	1,047	3,528
204	Grain Mill Products	389	1,177	1,140	406	3,202
205	Bakery Products	1,615	1,174	955	646	4,390
206	Sugar	16	26	72	68	182
207	Confectionary and Related Products	438	316	254	232	1,240
208	Beverages	1,038	1,144	1,517	677	4,376
209	Miscellaneous Foods and Kindred Products	897	1,124	1,619	858	4,498

Table A-2-3
Major Products and Annual Production for Meat Products

Major Product	Production/million lbs
Meat Packing Plant Products	
- Beef, not canned or made into sausage	17,866.5
- Pork, fresh and frozen	7,950.1
- Lard	1,848.9
Meat Processing Plant Products	
- Pork, processed or cured (not canned or made into sausage)	3,963.1
- Hams and picnics, except canned	1,349.7
- Sliced bacon	1,163.1
- Sausage and similar products (not canned)	4,254.6
- Frankfurters and weiners	1,158.8
- Other sausage, smoked or cooked (e.g., bologna, liverwurst, etc.)	1,649.8
- Canned meats (except dog and cat food) containing 20 percent or more meat	1,700.8
Poultry Dressing Plant Products	
- Hens (or fowl) and chickens	7,170.3
- Turkeys	1,564.1
- Canned poultry (sizes other than (1) 10 oz. and under or (2) 40.1 oz. to 60 oz.)	2,057.1

Table A-2-4
Major Products and Annual Production for Dairy Products

Major Product	Production/million lbs
Creamery butter, total	
National cheese (Italian, grated cheddar, brick, Swiss, etc.)	1,726.8
Dry milk products	2,852.9
(Dry skim milk)	(1,126.1)
Evaporated milk	1,618.2
Bulk fluid milk, and cream	15,830.3
(Fluid whole milk, bulk sales)	(11,689.7)
(Fluid skim milk, bulk sales)	(2,640.8)
Packaged fluid milk and related products, total	19,290.8
(Fluid whole milk packages)	(16,342.7)
(Partially skim milk, packaged; approximately 2 percent butterfat)	(1,346.5)
Buttermilk, chocolate drink, and other flavored milk products	1,214.9

Table A-2-5
Major Products and Annual Production for Canned and Preserved Fruits, Vegetables and Sea Foods

Part I Major Products	Production/1,000 Cases
Juices	9,400. +
Canned dry beans, total	69.900. +
Canned fruits (except baby foods), total	161,123
Canned vegetables (except hominy and mushrooms) total	243,164
Canned hominy and mushrooms, total	7,547
Apple juice	9,358
Grape juice (1,000 cases of 12)	6,407
Pineapple juice	11,960
Grapefruit juice	14,763
Orange juice, single strength	18,288
Grapefruit-orange juice blend	2,839
Grapefruit-pineapple juice blend	6,562
Prune juice (4,690 in 1,000 cases of 12)	8,718
Other whole fruit juice and mixtures of whole fruit juices	4,359
Nectars (including 1,000 cases of 40 and 12)	3,324
Fruit juices, concentrated, hot pack (including 1,000 cases of 48 and 1,000 gallons)	12,457
Canned vegetable juices, total	32,875
Catsup and other tomato sauces, total	96,680
Dietetic fruits	5,588.9

Part II Major Products	Production/million lbs
Dehydrated fruits, vegetables, and soup mixes, total	1,442.2
(Dried fruits and vegetables, except soup mixes)	(1,268.8)
Potato and potato products (french fries, patties, puff, etc.)	1,507.6
Frozen Specialties	2,369.8

Table A-2-6
Major Products and Annual Production for Grain Mill Products

Part I Major Products	Production/1,000 Sacks
Wheat flour, except flour mixes	245,703
Whole cornmeal	6,543
Degermed cornmeal	9,867
Corn grits and hominy except for brewer's use	7,454
Corn gruits and flakes for brewer's use	13,028
Cornmeal for animal feed	5,700
Other corm mill products (corn flour, etc.)	4,003
Rye flour	2,403
Other flour (excluding wheat, corn, rye)	3,577
Pancake and waffle mixes, total	2,994
Cake mixes, including gingerbread, total	9,305
Biscuit mixes, total	1,121
Cookie mixes, doughnut mixes and other sweet yeast goods mixes, total	6,290
Other prepared flour mixes, total	3,504
Part II Major Products	**Production/1,000 Short Ton**
Poultry feeds, including supplements	19,002
Livestock feeds, including supplements	20,123
Dog and cat food	2,300+
Dehydrated alfalfa meal	1,739
Cereal preparations, total	1,059
Milled rice, total	3,410

Table A-2-7
Major Products and Annual Production for Bakery Products

Major Products	Production/million lbs (Baked Weight)
Bread and bread-type rolls	14,371.4
Sweet yeast goods	1,025.1
Soft cakes, all types, including pound, layer, fruit, etc.	1,229.1
Crackers and pretzels	1,496.8
All other cookies and wafers excepting wafers for making ice cream sandwiches	1,448.6
	Production/millions of cones
Ice cream cones and cups	3,614.9

Table A-2-8
Major Products and Annual Production for Sugar Products and Confectionery and Related Products

Major Products	Production/1,000 short tons
Raw cane sugar	2,243.5
Refined cane sugar:	
Shipped in consumer units (cartons and sacks of 25 pounds or less)	1,873.3
Shipped in commercial units (bags and other containers more than 25 pounds)	1,227.0
Shipped in bulk (rail cars, trucks, or bins)	1,326.9
Beet sugar, total	4,611.9
Confectionery products, total	2,080+

Table A-2-9
Major Products and Annual Production for Beverage Products

Major Products	Production/1,000 bbl.
Malt liquors and brewing by-products:	
- Beer, cans (all sizes)	40,380
- Beer, returnable bottles (all sizes)	30,039
- Beer, nonreturnable bottles (all sizes)	18,576
- Beer, barrels and keys (all sizes)	16,980

Major Products	Production/million lbs
Malt, total	3,803.3

Major Products	Production/1,000 proof gallons
Whiskey (raw):	
- Bourbon	123,005
- Rye	5,129
- Other	10,948
Spirits (except fruit)	112,607
Other distilled liquors, including gin	33,327
Bottled in bond:	
- Whiskey	6,893
- Other	2,291

Major Products	Production/1,000 wine gallons
Rectified products:	
- Whiskey, blends of whiskey	2,560
- Whiskey, blends with neutral spirits and other whiskey	74,074
- Gin	1,969
- Cordials, liqueurs, cocktails, and similar compounds	21,627
- Vodka	16,296
- Other rectified products	3,165
Unrectified products:	
- Whiskey	79,906
- Gin	29,682
- Vodka	20,744
- Other unrectified products	4,164

Major Products	Production/1,000 cases
Soft drinks and carbonated water, total	1,759,900

Table A-2-10
Major Products and Annual Production for Miscellaneous Food Preparations and Kindred Products

Major Products	Production/million lbs
Cottonseed oil:	
- Crude	1,106.7
- Once-refined	1,128.0
Soybean oil	10,966.1
Soybean meal	26,425.2
Grease and inedible tallow	5,381.3
Meat meal and tankage	7,594.0
Shortening (baking and frying fats including bulk shipments of hydrogenated oils to bakers and fryers)	3,426.7
Hydrogenated oils other than baking or frying fats (for confectionery fats, mellorine fats, whipped topping, etc.)	1,220.0
Salad or cooking oil (fully refined and deodorized oil, produced at this plant)	3,204.7
Soybean cooking or salad oil (consumer and commercial sizes)	2,230.1
Margarine	2,125.6
Shortening (baking and frying fats)	2,670.2
Hydrogenated oils other than baking and frying fats	1,213.2
Salad or cooking oils, including olive oil (refined oils, bleached, deodorized, and/or unitized)	2,342.1

(4) Employment Statistics (Value Added) and Growth Patterns

Table A-2-11 shows the breakdown of employment statistics for the nine major classifications within the Food and Kindred Products industry (Reference 2).

Tables A-2-12 through A-2-16 depict the potential growth of production within this industry (Reference 3).

2. WASTE CHARACTERISTICS

The most serious problem of the Food and Kindred Products industry is water pollution. Since the raw materials of this industry are grown within our country, are processed here, and fulfill our most vital domestic consumption needs, it is important to be aware of the waste and waste sources that are inherent within the production processes. This section is concerned with the following subjects:

- Production Processes and Waste Sources
- Effluents to Air and Water
- Hazardous Waste Materials.

Table A-2-11
Detailed Employment Statistics for for SIC Codes 201-209 (Annual)

Item	SIC Codes								
	201	202	203	204	205	206	207	208	209
All employees (1,000)	310.1	231.7	259.9	111.8	264.2	30.9	83.1	220.7	137.0
Payroll for all employees (million dollars)	1,953.5	1,449.3	1,231.1	758.2	1,664.8	209.6	434.2	1,525.4	850.7
Production Workers (1,000)	248.7	107.3	226.7	77.9	159.6	24.9	68.7	113.5	94.3
Wages for all production workers (million dollars)	1,435.1	604.5	952.3	480.1	891.5	160.9	312.1	725.4	500.5
Man-hours of production workers (millions)	508.0	222.1	435.9	167.5	320.1	53.5	132.4	226.8	193.1
Value added by manufacture (million dollars)	3,551.0	3,466.4	3,588.2	2,881.9	3,494.6	652.0	1,248.0	4,790.1	2,948.7
Establishments:									
. with 1-19 employees	2,885	3,682	1,685	2,115	2,582	20	777	2,232	3,026
. with 20-99 employees	1,284	1,880	1,161	887	1,029	57	279	1,671	1,161
. with 100 employees or more	745	626	680	200	779	105	184	473	309

Table A-2-12
Projected Per Capita Food Consumption

		(Pounds, except for eggs)			
		1970	1980	1990	2000
Total calories per day		3,130	3,120	3,100	3,080
Total annual consumption (retail weight equivalent)		1,470	1,490	1,490	1,490
Meat, total (carcass wt.)	L	164	170	170	170
	M	175	187	190	195
	H	185	195	205	210
Beef (carcass wt.)	L	83	85	85	85
	M	95	103	105	105
	H	100	110	115	115
Veal (carcass wt.)	L	7.0	7.0	7.0	7.0
	M	7.8	8.5	9.0	9.0
	H	8.5	9.5	10.5	11.0
Lamb and mutton (carcass wt.)	L	3.7	3.5	3.5	3.5
	M	4.9	5.5	6.0	6.0
	H	6.0	6.5	7.0	7.5
Pork (carcass wt.)	L	60	60	60	60
	M	66	70	74	75
	H	78	83	85	85
Fish (edible wt. equiv.)	L	9	9	9	9
	M	10	10	10	10
	H	11	11	11	11
Poultry (ready-to-cook basis)	L	35	35	35	35
	M	38	40	40	40
	H	43	45	45	45
Eggs (number)	L	330	330	330	330
	M	360	360	360	360
	H	390	400	400	400

Table A-2-12
Continued

		(Pounds, except for eggs)			
		1970	1980	1990	2000
Dairy products (whole milk equiv.)	L	590	550	560	500
	M	645	630	610	610
	H	675	680	680	680
Milk Fat	L	22	20	18.5	18
	M	24	23	22	22
	H	25	25	24	24
Non-fat solids	L	44	44	44	44
	M	48	51	53	53
	H	51	56	58	58
Wheat (grain equiv.)	L	135	120	110	100
	M	145	135	125	120
	H	155	145	140	140
Corn (grain equiv.)	L	35	31	28	26
	M	39	35	32	31
	H	43	40	38	38
Potatoes and sweet potatoes (farm wt.)	L	95	85	85	85
	M	105	95	95	95
	H	120	115	115	115
Tomatoes (farm wt.)	L	70	70	70	70
	M	75	80	80	80
	H	83	88	90	90
Other vegetables (farm wt.)	L	175	175	175	175
	M	190	190	195	195
	H	205	210	220	220
Citrus fruit (farm wt.)	L	90	100	100	100
	M	105	115	115	115
	H	110	125	130	130
Apples (farm wt.)	L	22	20	20	20
	M	24	23	23	23
	H	26	25	25	25

Table A-2-12
Continued

		(Pounds, except for eggs)			
		1970	1980	1990	2000
Other fruits and melons (farm wt.)	L	105	101	100	100
	M	117	115	115	115
	H	125	125	125	125
Sugar and syrups (refined equiv.)	L	100	100	100	100
	M	105	105	105	105
	H	115	115	115	115
Fats and oils (retail wt.)	L	60	60	60	60
	M	65	65	65	65
	H	70	70	70	70
Coffee, tea, and cocoa (retail wt.)	L	15	15	15	15
	M	17	17	17	17
	H	19	20	20	20

Table A-2-13
Percentage of Food Energy Contributed by Major Food Groups

	1970	1980	1990	2000
Dairy products, excluding butter	14.0	14.4	14.7	14.8
Eggs	2.7	2.8	2.8	2.8
Meat, poultry, and fish	16.5	17.7	18.3	18.4
Fats and oils, including pork fat cuts and butter	20.2	20.3	20.4	20.6
Potatoes and sweet potatoes	2.7	2.5	2.5	2.5
Fruits, vegetables and nuts	9.9	10.2	10.3	10.3
Flour and cereal products	19.2	17.4	16.0	15.6
Sugar and syrups	14.8	14.8	14.9	15.0
	100.0	100.0	100.0	100.0

Table A-2-14
Aggregate Domestic Consumption of Principal Food Items

		(Billion pounds, except for eggs)			
		1970	1980	1990	2000
Beef (carcass wt.)	L	16.8	19.2	21.2	22.8
	M	19.8	25.2	30.1	34.8
	H	22.3	30.6	40.1	49.8
Veal (carcass wt.)	L	1.41	1.58	1.74	1.88
	M	1.62	2.08	2.58	2.98
	H	1.89	2.65	3.66	4.76
Lamb and mutton (carcass wt.)	L	.75	.79	.87	.94
	M	1.02	1.34	1.72	1.99
	H	1.22	1.81	2.62	3.25
Pork (carcass wt.)	L	12.2	13.6	14.9	16.1
	M	13.7	17.1	21.2	24.8
	H	17.3	23.1	29.7	36.8
Fish (edible wt.)	L	1.82	2.03	2.24	2.41
	M	2.08	2.45	2.87	3.31
	H	2.45	3.07	3.84	4.76
Poultry (ready-to-cook basis)	L	7.1	7.9	8.7	9.4
	M	7.9	9.8	11.5	13.2
	H	9.6	12.6	15.7	19.5
Eggs (billions)	L	66.7	75	82	88
	M	74.9	88	103	119
	H	87.0	112	140	173
Dairy products (whole milk equiv.)	L	119	124	127	134
	M	134	154	175	202
	H	151	190	237	294
Milk Fat	L	4.44	4.52	4.61	4.82
	M	4.99	5.64	6.31	7.28
	H	5.58	6.97	8.38	10.39

Table A-2-14
Continued

		(Billion pounds, except for eggs)			
		1970	1980	1990	2000
Non-fat solids	L	8.9	9.9	11.0	11.8
	M	10.0	12.5	15.2	17.5
	H	11.4	15.6	20.2	25.1
Wheat (grain equiv.)	L	27.3	27.1	27.4	27.0
	M	30.1	33.0	35.9	39.7
	H	34.5	40.4	48.9	60.6
Corn (grain equiv.)	L	7.07	7.01	6.97	6.97
	M	8.11	8.57	9.18	10.26
	H	9.59	11.16	13.26	16.45
Potatoes & sweet potatoes (farm wt.)	L	19.2	19.2	21.2	22.8
	M	21.8	23.3	27.3	31.4
	H	26.8	32.1	40.1	49.8
Tomatoes (farm wt.)	L	14.1	15.8	17.4	18.8
	M	15.6	19.6	23.0	26.5
	H	18.5	24.6	31.4	39.0
Other vegetables (farm wt.)	L	35.4	39.6	43.6	46.9
	M	39.5	46.6	56.0	64.5
	H	45.7	58.6	76.8	95.3
Citrus fruit (farm wt.)	L	18.2	22.6	24.9	26.8
	M	21.8	28.3	33.0	38.1
	H	24.5	34.9	45.4	56.3
Apples (farm wt.)	L	4.40	4.52	4.98	5.36
	M	4.99	5.64	6.60	7.61
	H	5.80	6.98	8.72	10.80
Other fruits and melons (farm wt.)	L	21.2	22.8	24.9	26.8
	M	24.3	28.2	33.0	38.1
	H	27.9	34.9	43.6	54.1
Sugar and syrups (refined equiv.)	L	20.2	22.6	24.9	26.8
	M	21.8	25.7	30.1	34.8
	H	25.6	32.1	40.1	49.8

Table A-2-14
Continued

		(Billion pounds, except for eggs)			
		1970	1980	1990	2000
Fats and oils (retail wt.)	L	12.1	13.6	14.9	16.1
	M	13.5	15.9	18.7	21.5
	H	15.6	19.5	24.4	30.3
Coffee, tea, and cocoa (retail wt.)	L	3.03	3.39	3.74	4.02
	M	3.54	4.16	4.88	5.63
	H	4.24	5.58	6.98	8.66

Table A-2-15
Projected Combinations of Per Capita Meat and Poultry Consumption

	(Pounds, carcass weight, for beef and veal, pork, lamb, mutton; ready-to-cook weight for poultry)			
	1970	1980	1990	2000
I. High total consumption, with emphasis on beef:				
Beef and veal	107	117	122	124
Pork	74	75	79	80
Lamb and mutton	4	3	4	6
Poultry	35	35	35	35
Total	220	230	240	245
II. High total consumption, with emphasis on variety:				
Beef and veal	101	105	113	118
Pork	78	83	85	85
Lamb and mutton	6	6.5	7	7.5
Poultry	35	35	35	35
Total	220	230	240	245
III. Medium consumption:				
Beef and veal	103	111	114	114
Pork	66	70	74	75
Lamb and mutton	4.9	5.5	6	6
Poultry	38	40	40	40
Total	212	227	234	235
IV. Low total consumption, with emphasis on beef:				
Beef and veal	100	107	107	107
Pork	60	60	60	60
Lamb and mutton	4	3	3	3
Poultry	43	45	45	45
Total	207	215	215	215

Table A-2-25
Continued

	(Pounds, carcass weight, for beef and veal, pork, lamb, mutton; ready-to-cook weight for poultry)			
	1970	1980	1990	2000
V. Low total consumption, with emphasis on variety:				
Beef and veal	91	95	95	95
Pork	68	70	70	70
Lamb and mutton	5	5	5	5
Poultry	43	45	45	45
Total	207	215	215	215

Table A-2-16
Projected Combination of Aggregate Meat and Poultry Consumption

	(Billion pounds carcass weight, for beef and veal, pork, lamb and mutton; ready-to-cook for poultry)			
	1970	1980	1990	2000
I. High total consumption, with emphasis on beef:				
Beef and veal	23.8	32.6	42.6	53.7
Pork	16.5	20.9	27.6	34.7
Lamb and mutton	.9	.8	1.4	2.6
Poultry	7.8	9.8	12.2	15.2
Total	49.0	64.1	83.8	106.2
II. High total consumption, with emphasis on variety:				
Beef and veal	22.5	29.3	39.4	51.0
Pork	17.4	23.2	29.7	36.8
Lamb and mutton	1.3	1.8	2.5	3.2
Poultry	7.8	9.8	12.2	15.2
Total	49.0	64.1	83.8	106.2
III. Medium consumption:				
Beef and veal	21.4	27.3	32.7	37.7
Pork	13.7	17.1	21.2	24.8
Lamb and mutton	1.0	1.3	1.7	2.0
Poultry	7.9	9.8	11.5	13.2
Total	44.0	55.5	67.1	77.7
IV. Low total consumption, with emphasis on beef:				
Beef and veal	20.2	24.2	26.6	28.7
Pork	12.1	13.5	14.9	16.1
Lamb and mutton	.8	.7	.8	.8
Poultry	8.7	10.2	11.2	12.1
Total	41.8	48.6	53.5	57.7

Table A-2-17
Continued

	(Billion pounds carcass weight, for beef and veal, pork, lamb and mutton; ready-to-cook weight for poultry)			
	1970	1980	1990	2000
V. Low total consumption, with emphasis on variety:				
Beef and veal	18.4	21.5	23.7	25.5
Pork	13.7	15.8	17.4	18.8
Lamb and mutton	1.0	1.1	1.2	1.3
Poultry	8.7	10.2	11.2	12.1
Total	41.8	48.6	53.5	57.7

(1) Production Processes and Waste Sources

Common to all raw products, the initial processes involve precleaning, size grading, and sorting. The purpose of these is to remove unwanted and undesirable material from food before it undergoes processing.

Wastes from this operation for canned and frozen fruits and vegetables often include soil, sand, stones, insecticides, dried plant juices, vegetation, insects, and other residues (Reference 4). The only waste within this group that might be hazardous is insecticides; however, the concentration is usually low. Trimming, coring and pitting, cutting, peeling, inspection and grading are also included in Initial Preparation. However, not all raw materials are processed by each of these steps. Whether the harvest was hand- or machine-picked(1) will effect the amount of impurities. These impurities are removed by soaking, spray rinsing, or air cleaning (limited use).

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(1) The trend is toward the machine-picked harvesting which produces more soil and other foreign matter wastes and, in turn, requires higher product specifications and more thorough cleaning.

These techniques produce large wastewater volumes and pollution loads. Size grading is usually done with screens, belts, or other separators. Sorting is usually a hand operation and primarily affects the quantity of solid wastes. Some liquid and solid wastes originate from trimming which is mainly a hand operation. Coring and pitting, generally a mechanical process, results in solid waste. The cutting and peeling operations produce a considerable volume of wastewater and high loads of BOD: cutting emits liquid waste from product juices and equipment wash water; peeling emits most wastes from the chemical peeling operation, although hand, steam, and machine operations are used. The lye peel rinse is highly alkaline, hot, and mineralized, and contains a considerable amount of dissolved organic matter. After grading and inspection, the final step in initial preparation is transportation to the Converted Product Handling processes. Transportation is usually accomplished by belt conveyors or flume. If flume water is discharged without extended reuse, it represents a large volume and percentage of the total wastewater, since it contains a significant amount of the total plant BOD and suspended solids.

These processes, plus plant cleanup from these operations, contribute about 50 percent of the total plant wastewater volume, a major portion of the plant BOD, and virtually all of the suspended solids.

The Converted Product Handling of canned fruits and vegetables involves some or all of the following processes: blanching, mixing and adding syrups and brine solutions, pulping, straining, cooking in vats, can filling, exhausting and sealing, thermo processing, can cooling and storage. The equipment and floors of this portion of the cannery are cleaned regularly, either at the end of each shift, or at the end of each day. The waste from blanching is hot and contains a considerable amount of dissolved organic matter. Only spillages or spoiled solutions cause waste during the process of mixing and adding syrups and brine solutions. Little waste originates from these processes except when the equipment is washed. However, when the pulp is wasted, as in the production of canned fruit juices, disposal of the pulp and strained solids becomes a solid waste problem. Insignificant quantities of waste result from the other processes with the exception of cooling. Since cans are usually cooled in water, considerable wastewater is generated.

The Converted Product Handling processes for frozen fruits and vegetables are categorized as blanching, washing, cooling, final preparation and inspection, packing, and freezing. The quantity of wastes from each operation, in terms of both flow and organic load, is variable and primarily a function of the raw product being processed. By far the most significant waste results from the blanching operation. The final steps in preparing frozen fruit juices are extraction, screening, deoiling, deaeration, pasteurization and concentration, packing and freezing. The extraction and screening processes are usually mechanical and result in tremendous quantities of solid residues and some liquid wastes. Deoiling is accomplished at the same time as deaeration and, if the steam used in the evacuator is condensed to avoid air pollution problems, a liquid waste containing dissolved contaminants results. Canning of juices requires several of the same processes as freezing, and the quantity and characteristics of the wastes are similar.

In seafood plants, primarily salmon, where delivered fish are flumed and/or refrigerated, the largest volume of wastewater is generated by the flumes and refrigeration tanks (Reference 5). However, sea water is used in these operations, during which time the characteristics of the water are not significantly altered. The largest volume of processing wastewater is from the rinse sprays provided at the end of the "iron chink." This flow, augmented by water used to flush the gutters, is used to convey product residuals deposited into the gutter system. Hoses used to clean the floors and equipment add significantly to the plant effluent. These streams are consolidated, generally in a central gutter, screened to remove solids, and discharged from the plant.

The major sources of wastewater from sardine processing are the delivery pumping system and pickling tanks. Fish scales are the only residuals contained in these streams. A significant quantity of processing wastewater is generated to hydraulically conveyed residuals. Flumes and gutters are continuously flushed, generally with sea water, to remove residuals from the processing areas. Condensate and fish oils from the steam rooms are added to the effluent.

Several shrimp processing operations contribute significantly to the wastewater volume. The water tanks where the shrimp are received are provided with a continuous overflow. Lubricating and cleaning sprays, used in peeling and deveining machines, contribute significant quantities of organic matter.

Washers provided after the cleaning and deveining operations discharge large volumes of wastewater. In addition, the vats used to blanch the shrimp contribute significantly to the organic load.

The major sources of wastewater from tuna processing are the flumes (conveying raw fish) and the thawing tanks. From the product preparation lines, the only continuous source of wastewater is from the fish washer at the butchering tables. Additional wastewater flows are discharged during the washing of tuna trays and racks, as well as the general plant cleanup.

In the meat packing industry, there are five processes which have a major impact upon the wasteload (Reference 6). These processes are as follows:

- Blood recovery—Either it is recovered, or it escapes to the sewer. Recovery means 42 percent reduction in the gross wasteload. Since blood is rich in protein, it is economically rational to recover it. However, the very small plant does not produce tankage and is not located in an area where it can sell raw blood; therefore, it usually dumps the blood into the sewer.

- Paunch handling—This material becomes a source of pollution problems if it is dumped into the sewer, since the total solids concentration becomes so large that it interferes with the efficient workings of the traditional waste treatment methods.

- Edible rendering—The most polluting and oldest method is wet rendering without evaporating tank water. The newer methods, dry rendering and low temperature rendering, cut wasteloads by 60 percent.

- Inedible rendering—The wet rendering method must be followed by evaporation of tank water in order to cut wasteloads in half. Both forms of dry rendering, batch and continuous, will produce 60 percent less wasteloads than the wasteloads from wet rendering systems without evaporation of tank water.

- Cleanup—The general practice of the industry is using water from high-pressure hoses to clean up. Pollution loads could be substantially reduced by the use of dry cleanup prior to the wet cleanup.

Within the dairy industry, the significant wastes derived from the fundamental butter process are skim milk from the separation process, and buttermilk from the churning operation (Reference 7). These waste products may be converted into valuable byproducts through evaporating the moisture and drying the residue to a powder form for human consumption and/or animal feed. If the skim milk and buttermilk are treated as wastes, they become a difficult waste problem because of the high protein and BOD content: skim milk has a BOD of 7.3 percent and buttermilk 6.4 percent. Less significant sources of wastes are:

- The spillage which occurs in normal processing and packaging operations
- The wastes incurred with cleaning equipment at the end of a day's operation
- Some clear water waste occurs in those plants which use water for once-through cooling in their refrigeration systems.

It should be noted that no water which comes in contact with butter during the manufacturing process may be reused because of the danger of contamination.

The significant waste from the fundamental cheese and fluid milk processes is whey. This waste product may be converted into valuable byproducts through evaporating the moisture and drying the residue to a powder form for human consumption and/or animal feed. As a waste, whey becomes a most difficult problem because of the high protein and acidic content. Approximately 54 percent of the solids in the raw material remains, resulting in a BOD of 3.2 percent. Less significant sources are the same three mentioned in the previous paragraph.

The condensed and evaporated milk process produces wastes from the miscellaneous spillage that occurs in normal processing and packaging operations, and the loss which occurs from cleaning equipment at the end of the day. In addition, the soaps and chemical cleaning solutions used in daily sanitation procedures contribute to water waste.

Wastes derived from the ice cream and frozen desserts process are the same three bulleted items mentioned earlier for the fundamental butter process.

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(2) Effluents to Air and Water

Exclusive of containers in which products from the Food and Kindred Products industry are packaged, the following table presents those items which are effluents to air and water. This list also describes the significant hazard at present (Reference 8). The first four item sections of Table A-2-17 include wastes from prunings, or as manure, crop residue, and garbage. These items are general wastes from two of the nine major industry classifications. The other item sections are Canning, Meat Animal Carcasses, Fish Products, Dairy, Brewery and Winery, and Sugar Refinery. These best examplify the types of production which produce air and water effluents.

(3) Hazardous Waste Materials

Table A-2-18 presents the chemicals in the hazardous wastes of the Food and Kindred Products industry. The materials and the chemicals created in the waste are itemized (Reference 8). The items are arranged according to similarity in chemical breakdown.

Table A-2-17
Effluents to Air and Water

Item	Air Effluent	Water Effluent
Cereal and Grain Products, Meat Trimmings and Wastes, Oils and Fats, Fruit, Vegetables, Egg Shells, Bones, Tree Leaves, Plants	1. CO_2, CH_4, volatile short-chain fatty acids, H_2S. mercaptans, N_2, NH_3, may escape into atmosphere 2. Odor nuisance 3. CO, CO_2 may appear in stack discharge as combustion product	CO_2, aldehydes, ketones, organic acids, phenol, NH_4^+, NO_2^-, NO_3^-, plus sulfates, phosphates, and carbonates may leach to groundwater
Manure	1. CO_2, CH_4, volatile short-chain fatty acids, H_2S, mercaptans, N_2, NH_3, may escape into atmosphere 2. Odor nuisance 3. CO, CO_2 may appear in stack discharge or combustion process	1. Leaching of nitrogen may lead to dangerously high NO_2^-, and NO_3^- levels in the groundwater 2. Contamination with leachates from stored manures can be major source of groundwater
Orchards and Groves, Vineyards	1. CO_2, CH_4, volatile short-chain fatty acids, H_2S, mercaptans, N_2, NH_3, may escape into atmosphere 2. Heavy air pollution resulting from open burning	CO_2, aldehydes, ketones, organic acids, phenol, NH_4^+, NO_2^-, NO_3^- may leach to groundwater

Table A-2-17
Continued

Item	Air Effluent	Water Effluent
Field Crops, Truck Gardens, Orchards	1. CO_2, CH_4, volatile short-chain fatty acids, H_2S, mercaptans, N_2, NH_3, may escape into atmosphere 2. Heavy in pollution resulting from open burning 3. Odor nuisance	CO_2, aldehydes, ketones, organic acids, phenol, NH_4^+, NO_2^-, NO_3^-, plus sulfates, phosphates and carbonates may leach to groundwater
CANNING		
Fruit (remains), Vegetables (remains)	1. CO_2, CH_4, volatile short-chain fatty acids, H_2S, mercaptans, N_2, NH_3, may escape into atmosphere 2. CO, CO_2 may appear in stack discharge as combustion products 3. Odor nuisances from decomposing cannery wastes	1. CO_2, aldehydes, ketones, organic acids, phenol, NH_4^+, NO_2^-, NO_3^-, plus sulfates, phosphates and carbonates may leach to groundwater 2. Plant pathogenic organisms in fruit and vegetable residues may be transported to groundwater
MEAT		
Meat (stockyards); Slaughterhouse and Packing Plant	1. CO_2, CH_4, volatile short-chain fatty acids, H_2S, mercaptans, N_2, NH_3, may escape into atmosphere 2. CO, CO_2 may appear in stack discharge as combustion products 3. Odor nuisance from decomposing wastes	1. CO_2, aldehydes, ketones, organic acids, phenol, NH_4^+, NO_2^-, NO_3^-, plus sulfates, phosphates and carbonates may leach to groundwater 2. Leaching of nitrogen may lead to dangerously high NO_2^-, and NO_3^- levels in the groundwater

Table A-2-17 (Continued)

Item	Air Effluent	Water Effluent
ANIMAL CARCASSES		
Beef and Dairy Herds Sheep Flocks Swine Herds Horse Herds Poultry Flocks	1. CO_2, CH_4, volatile short-chain fatty acids, H_2S, mercaptans, N_2, NH_3, may escape into atmosphere 2. Odor nuisances from decomposing wastes	1. CO_2, aldehydes, ketones, organic acids, phenol, NH_4^+, NO_2^-, NO_3^-, plus sulfates, phosphates and carbonates may leach to groundwater 2. Contamination with leachates from stored manures can be major source of groundwater pollution
FISH PRODUCTS		
Fish Wastes: Entrails Skins Scales	1. CO_2, CH_4, volatile short-chain fatty acids, H_2S, mercaptans, N_2, NH_3, may escape into atmosphere 2. CO, CO_2 may appear in stack discharges as combustion products 3. Odor nuisances from decomposing wastes	CO_2, aldehydes, ketones, organic acids, phenol, NH_4^+, NO_2^-, NO_3^-, plus sulfates, phosphates and carbonates may leach to groundwater

Table A-2-17 (Continued)

Item	Air Effluent	Water Effluent
DAIRY		
Milk Residues, Whey	1. CO_2, CH_4, volatile short-chain fatty acids, H_2S, mercaptans, N_2, NH_3 may escape into atmosphere 2. CO, CO_2 may appear in stack discharge as combustion products 3. Odor nuisances from decomposing wastes	1. CO_2, aldehydes, ketones, organic acids, phenol, NH_4^+, NO_2-, NO_3-, plus sulfates, phosphates and carbonates may leach to groundwater 2. A reservoir wastewater stream problem
BREWERY AND WINERY		
Spent Hops, Grains, Grape Pomace, Fermented Starches, Yeast and Bacterial Biomass	1. CO_2, CH_4 volatile short-chain fatty acids, H_2S, mercaptans, N_2, NH_3 may escape into atmosphere 2. CO, CO_2 may appear in stack discharges as combustion products 3. Odor nuisances from decomposing wastes	CO_2, aldehydes, ketones, organic acids, phenol, NH_4^+, NO_2-, NO_3-, plus sulfates, phosphates and carbonates may leach to groundwater
SUGAR REFINERY		
Beet Wastes and Pulp, Cane Wastes and Pulp, Evaporator Residue, Steffen House Concentrates, Beet Washings	1. CO_2, CH_4, volatile short-chain fatty acids, H_2S, mercaptans, N_2, NH_3 may escape into atmosphere 2. CO, CO_2 may appear in stack discharges as combustion products 3. Odor nuisances from decomposing wastes	1. CO_2, aldehydes, ketones, organic acids, phenol, NH_4^+, NO_2-, NO_3-, plus sulfates, phosphates, and carbonates may leach to groundwater 2. Pesticides contained in the beet washings may leach into the groundwater or drain off into surface water

Table A-2-18
Hazardous Waste Materials

Item	Chemical Waste Breakdown
Cereal and Grain Products	Protein
Meat Trimmings and Wastes	Sugars
Oils and Fats	Starches
Fruit	Cellulose
Vegetables	Fat
Egg Shells, Bones	Neutral Fats
Tree Leaves	Fatty Acids
Lawn Trimmings	Lignin
Plants	Cellulose
Manures	
Cattle Manure (average: 10.44 lb/1,000 lb cow-day 18% total solids 14.4% volatile solids)	Lignin (20%), cellulose (25%), hemicellulose (18%), fatty and other volatile acids (3.2% - includes butyric, valeric and caproic acids), protein, protein-diamines, NH_4, organic N-intermediates (total N, 3.79%), P_2O_5 (1.1%), $CaCO_3$ Pathogens (not necessarily present) Salmonella, Mycobacterium bovis, Brucella cabustus, Leptospira, E. coli, viruses
Swine Manure (average: 0.795 lb/100 lb. pig-day 19% total solids 15% volatile solids)	Lignin, cellulose, hemicellulose, protein, protein-diamines, NH_4, organic N-intermediates (total N, 5.4%), fatty and other volatile acids (5.8%), P_2O_5 (4.6%), K (2.1%), $CaCO_3$ Pathogens (not always present) Salmonella, Brucella suis, E. coli, viruses

Table A-2-18
Continued

Item	Chemical Waste Breakdown
Poultry Manure (average: 0.20 lb/5 lb. bird-day 25% solids 18% volatile solids)	Lignin, cellulose, hemicellulose, protein, protein-diamines, NH_4, organic N-intermediates (total N, 5.4%), fatty and other volatile acids (5.8%), P_2O_5 (4.6%), K (2.1%), $CaCO_3$ Pathogens (not necessarily present) Salmonella, E. coli, viruses
Sheep and Goats (total solids, 25%)	Lignin (22%), cellulose (19%), hemicellulose (18.5%), protein, protein-diamines, NH_4, organic N-intermediates (total N, 4.0%), fatty and other volatile acids, P (1.5% as H_3PO_4), K_2O (1.9%), $CaCO_3$ Pathogens (not necessarily present) Salmonella, Brucella melitensils, E. coli, Leptospira, viruses
Horse Manure (total solids, 25%-30%)	Lignin (14%), cellulose (28%), hemicellulose (23.5%), proteins (7%), protein-diamines, NH_4, organic N-intermediates (total N, 2%), P (5% as H_3PO_4), K_2O (1.5%), $CaCO_3$
Orchards and Groves Apple Apricot Cherry Peach Pear Plum Citrus Walnut Miscellaneous Fruits Vineyards	Leaves and wood (cellulose (55%), lignin (24%), pentosans (18%), nitrogen (2%)

Table A-2-18
Continued

Item	Chemical Waste Breakdown
Field Crops Corn Stalks Wheat and other Grain Stubble Sugar Cane Stalks Begasse Rice Hulls	Carbohydrates ((80%) (cellulose and sugars)), protein and fat (20%), lignin, trace elements
Truck Garden Cull Vegetables Vegetables Trimmings Cull Berries	Carbohydrates, protein, lignin, trace elements
Orchards Cull Fruit Green Drop	Carbohydrates, protein, lignin, organic acids, trace elements
Greenhouse and Nursery Vegetable Material Flowering Plant Residue	Celloluse, lignin, carbohydrates, trace elements
	Canning
Fruit Pulp Press Peelings Seeds Cull Fruit Oils Resins	Cellulose (55%), lignin (25%), PO_4 (as H_3PO_4, 3%), N (2%), K (as K_2), 4.0%) Plant pathogens
Vegetables Skins Cores Cobs Shulks Stalks Trimmings	Cellulose (60%), lignin (25%), N (2.5%), P_2O_5 (0.7%), K_2O (2.0%), S, Mg, ash (20%), trace metals, pesticide residues Plant pathogens

Table A-2-18
Continued

Item	Chemical Waste Breakdown
	Meat
Meat Stockyards Manure Wastes Feed	Lignin (20%), celluslose (25%), hemicellulose (18%), fatty and other volatile acids (3.2% - includes butyric, valeric, and caproic acids), protein, protein-diamines, NH_4, organic N-intermediates total N, 3.79%), P_2O_5 (1.1%), $CaCO_3$ Pathogens (not necessarily present) Salmonella, mycobacterium bovis, Brucella caburtus, leptospira, E. coli, viruses
Slaughtering and Packing Plant Manure Blood Casing Hair Paunch Manure Bones Grease Hooves, etc. Heads Feathers	Volatile matter (80% - 90%), total N (10%), fibrous protein, fatty acids, neutral fat, P_2O_5 (3.5%), K_2O (2.5%), C-14 (17%)
Beef and Dairy Herds Sheep Flocks Swine Herds Horse Herds Poultry Flocks	Proteins, fats, glycogen, P, and trace amounts of minerals
	Fish Products
Entrails Skins Scales	Protein, amino acids, oils, N, P, K (N + P 7.0%)

Table A-2-18
Continued

Item	Chemical Waste Breakdown
	Dairy
Milk Residues Whey	Proteins, casein, albumin, carbohydrates, lactose, fat, K, P, S
	Brewery and Windery
Spent Hops Grains (Culls and Residues) Oats Rye Wheat Corn Rice Grape Pomace Fermented Starches Yeast and Bacterial Biomass	Volatile solids (90%), lignin, cellulose, carbohydrates, N (3%), P (as H_3PO_4, 1%), K (as K_2O, 0.6%)
	Sugar Refinery
Beet Wastes and Pulp (Most of the pulp disposed of as livestock feedstuff)	Cellulose, lignin, N (0.4%), P (0.6%), K (as K_2O, 0.6%), Ca, Mg
Cane Wastes and Pulp	Cellulose, lignin, N, P, K
Evaporatory Residue	Hexoses, pentoses, sugar fragments, resins, oils, tar, trace elements
Steffen House Concentrate	Betaine, glutamine, assorted amino acids, KOH
Beet Washings	Soil, pesticides residues

3. WASTE DISPOSAL PROCESSES AND PRACTICES

The Food and Kindred Products industry is one the largest and most widespread industries within the U.S. economy. Some product segments of the industry, such as meat products and sea foods, exist in relatively confined geographical areas, whereas others, such as dairy products and canned and frozen fruits and vegetables, are found in almost every state.

Due to the wide variety of food products processed by the industry, there exists many different processing techniques and, consequently, many different waste disposal processes and practices. In spite of these differences, however, there are many waste treatment methods which are common to many, if not all, food processing industries.

The following sections describe current waste treatment processes to the food industry, highlighting those problems and processes unique to a particular industry segment. Examples are given of the composition of waste streams from various industry segments, and the relative efficiencies of waste treatment processes and current trends affecting these processes.

(1) Current Waste Treatment Processes

Waste treatment processes typical to many segments of the food industry are briefly described as follows.

- In-plant control consists chiefly of arranging processing operations in such a way that solids or excessively strong waste streams are isolated and handled separately. This is done in order to promote water conservation and reuse.

- Screening to remove solids is one of the most common methods of pretreatment of food processing waters. Coarse screening is done with bar racks and fine screening with 10 to 40 mesh. There are a number of arrangements of fine mesh screening; the principal ones consist of disc screen, rotating drum, and vibrating type screen.

- Grease recovery is necessary for food processors who handle a significant quantity of meat or poultry. Free floating grease can be removed by means of the simple trap, or surface skimming, and is recovered as a marketable by-product. Emulsified grease tends to stay in suspension and is removed and recovered through air flotation and vacuum flotation systems, sometimes with the addition of chemicals such as alum, activated silica, chlorine,and other coagulant aids.

. Biological treatment involves the use of microorganisms to remove the organic materials by adsorption and direct metabolism. Biological oxidation yields carbon dioxide and water as end products and is achieved by the following processes.

- Trickling filters
- Activated sludge
- Oxidation ditch
- Lagooning
- Anaerobic digestion
- Spray irrigation

. Trickling filters are frequently used to treat organic wastes. These consist of racks, stacked 4 to 7 feet deep, over an underdrainage system. More recently plastic filter media have brought about more efficient systems through higher stacking, increased surface area and savings in land area. In either system, a gelatinous film of microorganisms develops on the filter media which adsorbs the soluble colloidal organics. Depending upon the composition of the wasteload, certain precautions must be observed to ensure sufficient microbial growth on the filter.

- Activated sludge process consists of adding a biologically active sludge to the wastewater and then aerating vigorously to supply the organisms with sufficient oxygen. The variety of activated sludge processes include the following.

  - Step aeration process
  - Contact stabilization process
  - Modified aeration process
  - Completely mixed process
  - Oxidation ditch process

- Lagoons consist both of storage and flow-through lagoons. Most frequently utilized, particularly in meat packing and food processing plants, is the combination of anaerobic and aerobic lagoons. Some lagoons rely strictly on natural conditions for reoxidation, others achieve increased loading with mechanical aeration.

- Spray irrigation involves the spraying of effluent over a prepared disposal field with a vegetative cover such as grass. Purification is accomplished biologically and is dependent upon the biota and organic litter on and in the soil.

- Anaerobic digestion treatment process is well suited to wastes of high organic content such as those from the meat packing industry. This process involves the heating of an entire stream of waste to 95°F and holding it in an anaerobic digester for about 12 hours.

Solids disposal has become a mounting problem for the food industry. For those materials that have no economic recovery value, there is a constant cost escalation for disposal. Various methods and associated problems for solids disposal include:

- Incineration - creates air pollution.

- Landfill and land spraying - limited by available land and high cost of material hauling to suitable locations.

- Quick composting - results in a humus which is a satisfactory soil conditioner; however, suitable markets for the conditioner are not always available.

- Ocean dumping - grinding and dumping from barges beyond a 26 mile point from the nearest mainland point are available only for food produced near a coast.

Industry sources indicate that the most satisfactory waste disposal process would involve the creation of new by-products from food processing. Until research chemists and engineers are able to create economical by-products, however, it appears that most food processing wastes will have to be treated as garbage and hauled away at considerable expense.

(2) Extent of Utilization of Waste Treatment Processes

The waste treatment processes available to the food industry are utilized to varying extents by different subclassifications within the industry. Since data is not available for all industry subclassifications, those industries for which data is available will be used to illustrate broad industry trends.

Generally, the food industry utilizes increasing amounts of waste treatment for its various effluents. However, the trend has been to make increasing use of municipal waste treatment facilities for waste treatment after certain basic in-plant treatments. The following table illustrates this trend for meat products, dairy products and canned and frozen fruits and vegetables.

Industry Classification	% Wastes Discharged to Municipal Sewers Year 1950	1963	1967	1972	1977
201 Meat Products	35	50	70	80	85
202 Dairy Products					
2021 Creamery Butter	1	5	10	32	53
2022 Cheese	1	5	10	32	53
2023 Condensed & Evap. Milk	1	5	10	32	53
2024 Ice Cream	50	70	80	90	98
2026 Fluid Milk	50	70	80	90	98
203 Canned & Frozen Fruits & Vegetables	50	60	62	65	69

Tables A-2-19 and A-2-20 illustrate the trend toward increased use of available treatment processes within the meat products and dairy industries. Since 1950, the total percentage of plants employing some type of treatment has increased considerably, such that at present virtually every meat and dairy products plant employs some type of processing prior to discharge at municipal sewers or watercourses.

(3) Efficiency of Waste Treatment Processes

Of the various waste treatment processes employed in the food industry, the two which have probably received the greatest attention are not those normally thought of as waste treatment at all. These include byproduct utilization and management technique. Both of these techniques reduce the quantities of waste prior to the implementation of standard treatment processes.

Table A-2-19
Utilization of Waste Treatment Processes in the Meat Products Industry

Type of Waste Treatment Facility	Estimated Percentage of Plants Employing Waste Treatment Process				
	1950	1963	1967	1972	1977
"Catch Basin" Only (Sedimentation and Grease Skimming)	60	50	46	10	10
Air Flotation	0	5	8	20	20
It is assumed that a "catch basin" will precede the following methods of treatment.					
Lagoon Systems	10	15	17	20	14
Trickling Filter	1	3	3	3	2
Activated Sludge	1	2	3	3	1
Anaerobic Contact (Followed by Lagoons, Activated Sludge, or Trickling Filter)	0	5	6	20	25
Channel Aeration (Pasveer Process)	0	0	2	5	10
Joint Industrial	0	1	2	10	15
Other (Including Chemical Treatment)	8	4	4	8	2
TOTAL (Plants With Some Type of Treatment Facility	80	85	91	99	99
No Treatment Facilities	20	15	10	1	1
TOTAL	100	100	100	100	100

Table A-2-20
Utilization of Waste Treatment Practices in the Dairy Industry

Treatment Process	% of Plants Employing Listed Processes				
	1950	1963	1967	1972	1977
Ridge and Furrow	U*	8	10	15	15
Spray Irrigation	U	5	5	5	5
Aerated Lagoon	U	5	10	15	25
Trickling Filter	U	U	U	U	U
Activated Sludge	U	U	U	U	U
Municipal Sewer	U-70	5-75	10-80	32-90	53-98
To Waterways	26-98	21-73	16-58	6-30	0
Utilization as By-product**	50	90	95	99	100
Management Technique	40	50-55	60-65	65-75	70-85

*U = Under 1%

**Condensed and Evaporated Milk and Ice Cream and Frozen Desserts have little by-product utilization.

By-product utilization entails the production of marketable by-products from residual material remaining after processing the primary product. This practice is particularly applicable in the meat products industry where virtually every part of the animal is utilized. The dairy products industry also has a high level of by-product utilization. Since by-products recovery is basically a form of raw materials conservation, it retains a high level of popularity throughout the food industry. In addition, it reduces the wasteload.

Management technique is also a form of conservation since it involves the closest possible supervision of production processes in order to reduce or eliminate processing losses at their source. This has been of particular benefit to the dairy products industry.

Tables A-2-21 through A-2-23 illustrate the efficiencies of various waste treatment processes. For most of these processes, the efficiency is limited by the nature of the process itself. However, the effective efficiency, as they are actually employed, is also dependent upon the composition of the waste streams which they must process. Processes such as spray irrigation and aerated lagoons have very high efficiencies, but are often limited by land availability and by sometimes having a sludge residue which must be disposed of.

(4) Net Annual Wasteloads and Waste Reduction

Fifteen-year net wasteload standards and projections for several food industry classifications indicate a gradual diminishing of net wastes discharged to watercourses. In all instances for which data is available, the gross wasteload in terms of

Table A-2-21
Efficiency of Waste Treatment Processes in the Meat Products Industry

Treatment Method (1)	Theoretical Waste Reduction % BOD Removed	% of Plants Employing Method of Waste Treatment	Gross Pollution Removed by Treatment mil lbs BOD (2)
"Catch Basin" only	25	50	135
Air Flotation Unit	50	5	27
Lagoons . Aerobic and Facultative (80) . Anaerobic (80) . Anaerobic-Aerobic (94)	90	15	146
Trickling Filter	90	3	29
Activated Sludge	95	2	21
Channel Aeration	80-95	0	0
Anaerobic Contact Plus . Trickling Filter . Activated Sludge . Lagoons	95	5	48
Other (including Chemical and Joint Industrial)	70	5	38
TOTAL		85	444

(1) All treatment methods except the "catch basins only" and "air flotation" are assumed to be preceded by "catch basins."

(2) Gross pollution load is 1082 million pounds of BOD.

Table A-2-22
Efficiency of Waste Treatment Processes in the Dairy Industry

Removal Method	Normal Removal Efficiency % of Total Wasteload Removed		
	Product	Soap & Chemicals	Wastewater
Ridge and Furrow	95-100	95-100	4*
Spray Irrigation	95-100	95-100	5*
Aerated Lagoon	90-95	90-95	1*
Trickling Filter	90-95	90-95	0
Activated Sludge	90-95	90-95	0
Municipal Sewer	100	100	100
To Waterways	100	100	100
Utilization as By-product	99.5	NA	99.5
Management Technique	50-75	40-75	10-75

*Estimated percent of total evaporated to the atmosphere.
The remainder goes to waterways.

Table A-2-23
Efficiency of Waste Treatment Processes in the Canned and Frozen Fruits and Vegetables Industry

Method	POLLUTION REDUCTION (%) Flow to Surface Water	BOD to Surface Water	SS to Surface Water
Screening 20-40 Mesh	0	0-10	56-80
Wet Oxidation	-	-	-
Sedimentation	0	10-30	50-80
Flotation	0	10-30	50-80
Chemical Precipitation	0	39-89	70-90
Chemical Oxidation	-	-	-
Activated Sludge	0	59-97	90-95
Trickling Filtration	0	36-99	85-90
Anaerobic Fermentation	0	40-95	-
Lagooning	0-50	83-99	50-99
Spray Irrigation	50-100	100	100
Sand Filtration	50-100	15-85	100

BOD, SS and TDS shows a steady increase from 1963 through 1977. However, significantly improved removal processes have more than compensated for the increase in wasteload. In most instances, wastes reaching watercourses are materially reduced as demonstrated in Tables A-2-24 through A-2-26.

Table A-2-24
Summary of Projected Net Wasteloads for the Meat Products Industry

Year	Gross Wasteload (million lbs BOD	Removal[1] %	Net Waste Discharged to Watercourses (million lbs BOD)
1963	1082	58	454
1968	1128	74	296
1969	1150	76	274
1970	1176	79	242
1971	1197	81	225
1972	1221	84	198
1977	1226	88	147

(1) Includes both in-plant and municipal treatment as well as process changes and by-product utilization.

Table A-2-25
Summary of Projected Net Wasteloads for the Dairy Industry

Year	Industry Classification	Gross Wasteload (million lbs BOD)	Removal[1] %	Net Waste Discharged to Watercourses (million lbs BOD)
1963	2021	4,142	85	629
	2022	515	53	242
	2023	25	16	21
	2024	18	78	4
	2026	176	80	35
1968	2021	3,716	91	340
	2022	606	58	254
	2023	20	30	14
	2024	20	85	3
	2026	196	87	25
1970	2021	3,309	93	271
	2022	619	67	204
	2023	20	50	10
	2024	20	90	2
	2026	198	91	18
1972	2021	3,931	95	199
	2022	640	79	142
	2023	19	68	6
	2024	20	90	2
	2026	201	95	10
1977	2021	4,243	99.5	22
	2022	705	96	30
	2023	17	99.5	less than 1
	2024	20	99.5	less than 1
	2026	208	99.5	less than 1

[1] Includes both in-plant and municipal treatment as well as process changes and by-product utilization.

Table A-2-26
Summary of Projected Net Wasteloads for the Canned and Frozen Fruits and Vegetables Industry

Year	Waste	Gross Wasteload (million lbs)	Removal[1] (%)	Net Quality Discharged to Watercourses (million lbs)
1963	BOD	370	57	160
	SS	425	63	160
	TDS	395	12	350
1968	BOD	435	64	155
	SS	500	73	135
	TDS	465	19	375
1969	BOD	445	65	155
	SS	510	74	135
	TDS	475	19	385
1970	BOD	455	66	155
	SS	520	75	130
	TDS	485	19	390
1971	BOD	460	67	150
	SS	525	76	125
	TDS	490	19	395
1972	BOD	465	68	150
	SS	535	77	125
	TDS	495	19	400
1977	BOD	490	73	130
	SS	565	82	100
	TDS	525	21	415

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(1) Includes both in-plant and municipal treatment as well as process changes and by-product utilization.

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APPENDIX A-3

SIC 22 — TEXTILE MILL PRODUCTS

1. INDUSTRY DESCRIPTION

Textile Mill Products is the title for Standard Industrial Classification (SIC) Major Group 22. This group is subdivided into the following categories:

221 - Broad Woven Fabric Mills, Cotton

222 - Broad Woven Fabric Mills, Man-Made Fiber and Silk

223 - Broad Woven Fabric Mills, Wool (Including Dyeing and Finishing)

224 - Narrow Fabrics and Other Smallwares Mills (Cotton, Wool, Silk, and Man-Made Fiber)

225 - Knitting Mills

226 - Dyeing and Finishing Textiles, Except Wool Fabrics and Knit Goods

227 - Floor Covering Mills

228 - Yarn and Thread Mills

229 - Miscellaneous Textile Goods.

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To establish a manageable scope for dealing with the wastes from the textile mill industry, it is desirable to concentrate on the processes within the production of the three principal types of textiles produced which contribute the most wastes posing the greatest hazard to the public health and welfare.

These textiles and processes with their corresponding SIC codes are described in the following paragraphs.

(1) SIC 2231—Wool Textile Weaving and Finishing

This industry includes those establishments primarily engaged in weaving fabrics over 12 inches in width, wholly or chiefly by weight of wool, mohair, or similar animal fibers; those dyeing and finishing woven wool fabrics or dyeing wool, tops, or yarn; and those shrinking and sponging wool goods for the trade. Establishments primarily engaged in weaving or tufting wool carpets and rags are classified under other codes.

(2) SIC 2261—Cotton Textile Finishing

This industry includes establishments primarily engaged in finishing purchased cotton broad woven fabrics, or finishing such fabrics or a commission basis. These finishing operations include bleaching, dyeing, printing (roller, screen, flock, plisse), and other mechanical finishing such as preshrinking, calendering, and napping. This code also includes the shrinking and sponging of cloth for the trade, and chemical finishing for water repellency, fire resistance, and mildew proofing.

(3) SIC 2262—Synthetic Textile Finishing

This industry includes establishments primarily engaged in finishing purchased manmade fiber and silk broad woven fabrics or finishing such fabrics on a commission basis. These finishing operations include bleaching, dyeing, printing (roller, screen, flock, plisse), and other mechanical finishing such as preshrinking, calendering, and napping.

(4) SIC 2269—Finishing of Other Textiles

This industry includes establishments primarily engaged in dyeing and finishing of textiles in forms other than broad woven fabrics such as finishing of raw stock, yarn, braided goods, and narrow fabrics, except wool and knit fabrics. These finishing operations include bleaching, dyeing, printing, and finishing. Establishments classified under this code perform finishing operations on purchased textiles or on a commission basis.

(5) Distribution of Establishments

Table A-3-1 shows the distribution of establishments included in the SIC codes being considered throughout the various states. The number of employees and the value added is also given by state.

Figure A-3-1 provides a graphic presentation of the relative distribution of major textile mills throughout the United States.

2. MAJOR RAW MATERIALS, ANNUAL PRODUCTION, AND INDUSTRY GROWTH PATTERN

(1) SIC 2231—Wool Textile Weaving and Finishing

The American wool market was reasonably stable and approximated about 400 million clean pounds or roughly 10 percent of the total fibers consumed annually by the U.S. textile industry in 1966. Industry 2231 shipments of woven wool fabrics in 1967 represented 96 percent of these products valued at $896.6 million shipped by all industries.

Wool mixtures in blend with synthetics and even cotton are becoming increasingly popular because of their reduced

Table A-3-1
1967 Census of Manufacturers Data

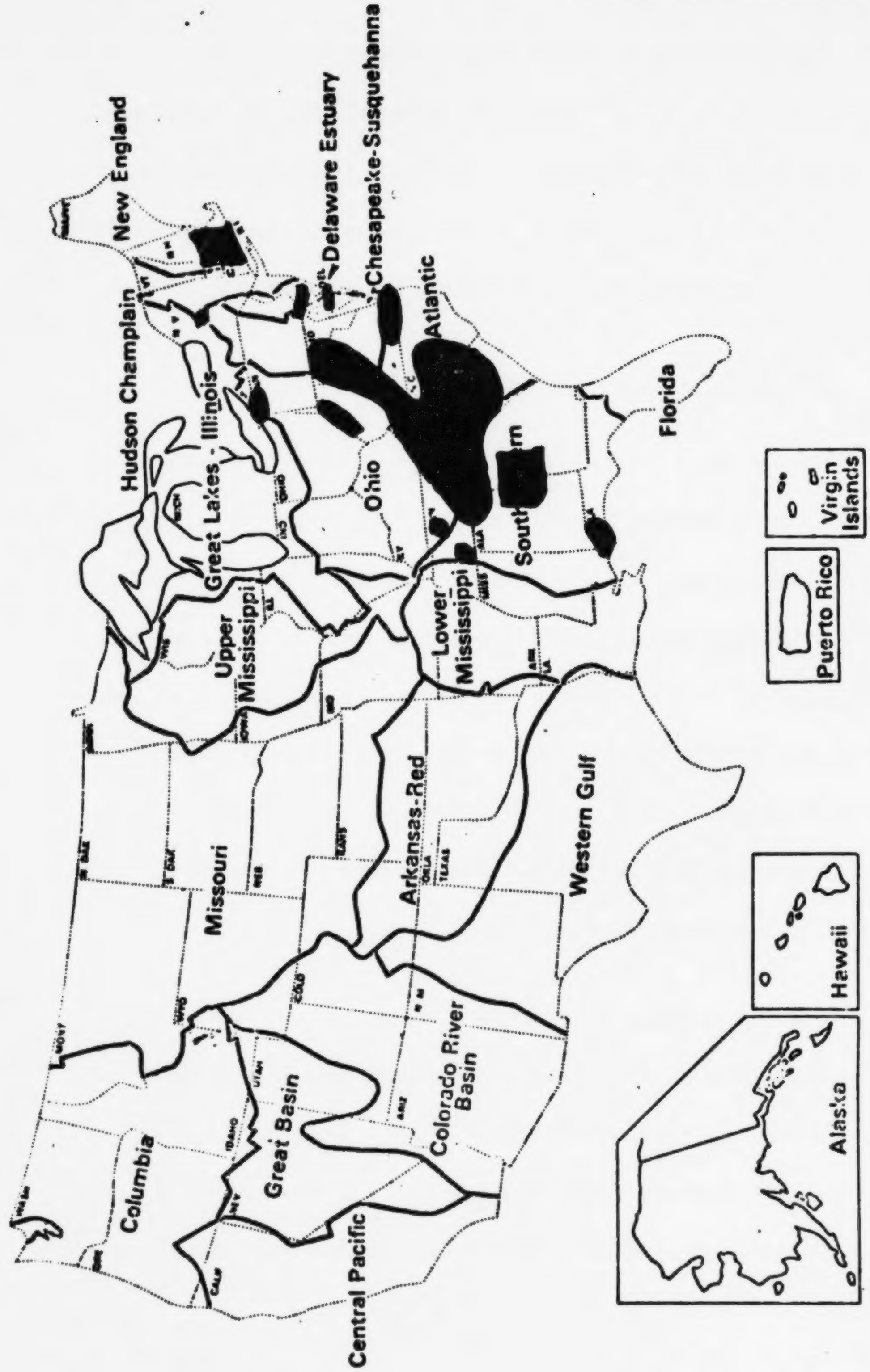
Industry and Geographic Area	Establishments		Number of Employees (1000)	Value Added By Manufacture (million dollars)
	Total Number	With 20 Employees Or More		
SIC 2231 - Weaving & Finishing Mills, Wool				
United States	310	217	41.8	428.6
New England Division	127	100	16.3	144.4
Middle Atlantic Division	89	48	5.9	63.1
East North Central Division	12	7	.9	7.8
West North Central Division	10	7	.5	3.7
South Atlantic Division	43	38	15.0	178.4
East South Central Division	7	5	1.0 - 2.499	(D)
West South Central Division	2	2	< .25	(D)
Pacific Division	18	10	1.0 - 2.499	(D)
SIC 2261 - Finishing Plants, Cotton				
United States	216	136	35.7	313.8
New England Division	37	27	4.2	35.6
Middle Atlantic Division	88	43	3.6	35.7
East North Central Division	14	4	.25 - .499	(D)
South Atlantic Division	54	49	24.1	211.4
East South Central Division	8	7	> 2.5	(D)
West South Central Division	5	3	0.25 - 0.50	(D)

Table A-3-1
Continued

Industry and Geographic Area	Establishments		Number of Employees (1000)	Value Added By Manufacture (million dollars)
	Total Number	With 20 Employees Or More		
SIC 2262 - Finishing Plants, Synthetics				
United States	233	167	25.7	271.4
New England Division	43	35	>2.5	(D)
Middle Atlantic Division	134	89	8.7	98.8
South Atlantic Division	45	38	>2.5	(D)
East South Central Division	1	1	<0.25	(D)
Pacific Division	5	2	0.5 - 1.0	(D)
SIC 2269 - Finishing Plants, NEC				
United States	192	105	12.3	124.8
New England Division	18	13	1.0 - 2.50	(D)
Middle Atlantic Division	103	40	2.8	27.8
East North Central Division	10	6	1.0 - 2.50	(D)
South Atlantic Division	46	39	>2.5	(D)
East South Central Division	10	6	1.0 - 2.50	(D)
Pacific Division	7	3	0.3	2.5

APPENDIX A-3-7

FIGURE A-3-1
Location of Major Fiber & Finishing Industries — Textile Mill Products


New England
Hudson Champlain
Delaware Estuary
Chesapeake-Susquehanna
Atlantic
Great Lakes - Illinois
Ohio
South
Florida
Upper Mississippi
Lower Mississippi
Missouri
Arkansas-Red
Western Gulf
Great Basin
Colorado River Basin
Columbia
Central Pacific
Virgin Islands
Puerto Rico
Hawaii
Alaska

cost, improved weight, washability and wear, and other characteristics. The influence of recent synthetics competition has assisted in stimulating some technological advancement into the wool processing industry. There appears to be a trend toward larger plants to replace older, less efficient operations.

(2) SIC 2261—Cotton Textile Finishing

Cotton fiber is the single most popular and important fiber in the American textile industry. Its excellent absorptive and use characteristics, as well as reasonable price, contribute to the stable market of about 7 to 9 million bales per year consumed during the past decade; this quantity represents approximately one-half of the total fiber used by our textile industry. SIC 2261 shipments of cotton broad woven fabric finishing in 1967 represented 58 percent of these products valued at $1,087.0 million shipped by all industries.

Cotton mixtures in blend with synthetics are becoming increasingly popular because of the resulting cost, appearance, and utilitarian features. The U.S. cotton industry has been traditionally dependent on low labor costs to meet competition from abroad. Presently, industry leaders are developing newer, more efficient, larger production yield equipment to replace the older, less efficient subprocess facilities in order to overcome domestic labor problems, synthetic fiber, and expanding foreign competition. It is also interesting to observe that cotton production has partially shifted from the Southern United States into the irrigated lands of the Western United States. The United States exported over 5 million bales of cotton in 1964 alone. The cotton industry is expanding in both research and promotion in order to compete with the well publicized synthetic fibers.

(3) SIC 2262—Synthetic Textile Finishing

Synthetic fibers (namely, those fibers which are man-made and not found in nature) fall into two main groups, i.e., those produced from cellulose and those produced synthetically from organic materials. The cellulose fibers are principally rayon and acetate. The cellulosic fibers make up approximately 6 percent of the last decade's fiber consumption. The organic fibers are principally acrylics, polyesters, and nylon. Noncellulosic synthetic fibers have markedly increased their annual domestic consumption from approximately 3 million cotton-equivalent bales in 1957 to some 6 million bales equivalent in 1966.
SIC 2262 shipments of manmade fiber and silk broad woven

fabric finishing in 1967 represented 45 percent of these products, valued at $1,022.7 million, shipped by all industries.

The organic synthetic fiber industry is the most rapidly growing segment of the textile industry and is continually creating new and varied fibers to add to the already large number of synthetic fibers now on the market.

(4) SIC 2269—Finishing of Textiles Other Than Broad Woven Fabrics

This industry is comprised of establishments primarily engaged in the finishing of cotton and synthetic textiles which are not in the broad woven form. Raw stock, yarn, braided goods, and narrow fabrics are the primary products of this industry. This industry's 1967 shipments represented 52 percent of these products, valued at $350.4 million, shipped by all industries.

3. PRODUCTION PROCESSES AND WASTE CHARACTERISTICS

The production finishing processes and associated wastes discussed in this section apply to the wool, cotton, and synthetic fiber industries.

As a general rule, there are four basic subprocesses involved in the finishing of textiles:

- Scouring
- Dyeing and/or printing
- Bleaching
- Special finishing.

Special finishing is meant to include all subprocesses which cannot be classified in one of the preceding three categories.

(1) Wool Industry

1. Production Processes

Raw sheep wool receives a preliminary wash and rinse. Then, the fairly clean wool is carbonized with acid and heating to remove the residual waste. After another washing, the fibers are ready for carding, fulling, and weaving. They can be dyed either before or after weaving.

The fundamental processes in the production of finished wool are scouring, dyeing, carding, fulling, washing, carbonizing, and bleaching. Although fulling discharges little direct waste, it contributes to the total wasteload by the addition of biodegradable chemicals which are removed in the washing process. Except for carding, all of the remaining processes are direct sources of waste.

For each of the fundamental processes, three levels of technology are described:

- Older technology (new in 1950)
- Prevalent technology (new in 1963)
- Newer, more advanced technology (new in 1967).

(1) Scouring

Older technology scouring — Grease wool is scoured in a 3 to 5 bowl scouring train or in 3 to 5 separate bowls in which wool is washed in batches. Soap and soda ash are used in the first 2 or 3 bowls with clean water in the remaining bowls. The last bowl is a continuously running overflow rinse which is not recirculated or reused in any way.

Prevalent technology scouring — Depending on the size of the plant, grease wool is initially scoured in a 3 to 5 bowl train using a low BOD (12 percent

OWC (Other Weight Chemical)) synthetic detergent in the first 2 or 3 bowls. The rinse water from the last bowl (or bowls) is recirculated in a counterflow operation.

Newer technology scouring—The grease wool is packed into large vacuum kiers and scoured with methyl alcohol to remove suint salts. The wool is then scoured with isopropyl or ethyl alcohol to remove grease. The spent solvent can be distilled for reuse and grease recovery. Finally, the wool is washed in water to remove dirt and other soluble particles remaining on the fiber.

(2) Stock Dyeing

Older technology stock dyeing—Dyeing is done in sunken open top kettles containing acetic acid (62 percent OWC BOD) and dye solution. The wool is placed in wire mesh baskets with slow moving paddles and immersed in the solution.

Prevalent technology stock dyeing—The scoured wool is normally stock dyed in pressure kettles using ammonium sulfate or sulfuric acid and sodium sulfates, plus dye solution. The type of dye used depends on the color desired, fastness to light and water, and other properties.

New technology stock dyeing—Scoured wool is stock dyed by a continuous process using pressure equipment similar to a scouring train but with eight compartments and automatic controls to prevent or control felting. Ammonium sulfate and dye solution are used in various concentrations in the compartments.

(3) Carding

Older technology carding—Due to shortages, low BOD carding oils were developed during World War II and were found to be as good as, or better than, olive oil. Further improvements in these synthetic oils had made their use normal practice by 1950.

Prevalent technology carding—A low BOD oil (approximately 20 percent OWC) is sprayed onto the fiber while it is being mixed, in amounts ranging from 1 to 8 percent. The fiber is then drawn, spun, and woven into cloth.

Newer technology carding— Low BOD carding oils (less than 3 percent OWC) are added in amounts of 1 to 8 percent OWC.

(4) Fulling

Older technology fulling— Soap is generally used as a fulling agent, often mixed with small amounts of soda ash. The cloth is immersed in the fulling solution then passed through squeeze rollers which remove most excess.

Prevalent technology fulling— The wool cloth is passed through an impregnating box containing a synthetic fulling agent of low BOD (about 12 percent OWC). The amount added (amount remaining in cloth) depends on the degree of felting desired, and usually falls in a range of 5 to 10 percent OWC.

Newer technology fulling— The fulling agents used are either synthetic chemicals or sulfuric acid, hydrogen peroxide combinations. Fulling is still done in tubs with beating action rollers. This type of equipment has been in use for many years.

(5) Washing

Older technology washing—Soap and soda ash plus softening agents are used in the string washer in which approximately 46,000 gallons of water are used for each 1,000 pounds of wool. Rinse water is generally not reused.

Prevalent technology washing—A low BOD (12 percent OWC) synthetic detergent is used in a string washer in which the entire wash-rinse cycle is carried out twice to ensure complete removal of the oil and fulling agent. Some of the rinse water is recirculated and used to make the detergent solution.

Newer technology washing—The fulling solution is completely neutral and contributes no BOD in itself. Spray rinsing with recirculation or a running rinse in a continuous piece washer may be used.

(6) Carbonizing

Older technology carbonizing—Carbonizing is done with a 6 percent sulfuric acid solution and 212°F oven. Crushing and dusting are done mechanically and neutralization is achieved by immersion in a soda ash solution. The wool is rinsed before and after neutralization with 16,000 ± gallons of water/1,000 pounds of wool.

Prevalent technology carbonizing— The wool is carbonized with a 6 percent sulfuric acid solution and oven heating to 212°F. It is neutralized by soaking in a soda ash solution followed by a running rinse of 16,000 gallons/1,000 pounds of wool.

Newer technology carbonizing— Traditional methods of carbonizing have not been improved to the extent of reducing the pollution loads; however, some water reuse in rinsing may be practiced.

(7) Bleaching and Piece Dyeing

Older technology bleaching and piece dyeing— Bleaching is done in the dye kettles generally using hydrogen peroxide. This usually requires heating to 115°F for at least 3 hours in order to obtain a good bleach. Piece dyeing is rare, but the procedure and process chemicals are similar to those used for stock dyeing of wool fibers.

Prevalent technology bleaching and piece dyeing—The small percentage of wool cloth which is to remain white is bleached with sulfur dioxide or hydrogen peroxide in vats which are also used for dyeing. Some plants may bleach in the last bowl of the scouring train before the fiber is woven. Optical brightening, using acetic acid and fluorescent organic compounds, is used in many mills. Some mills may do a small amount of dyeing in small dye lots following all finishing processes.

Newer technology bleaching and piece dyeing—Traditional methods of bleaching and piece dyeing are followed in newer, technologically advanced plants.

2. Waste Characteristics

The major sources of polluting wastes in the wool yarn and textile production process are scouring, dyeing, and washing.

Of all the textile wastes, wool scouring wastes are generally considered the most difficult to treat. Raw wool contains an average of about 50 percent impurities and fibers. Approximately 50 percent of these impurities are wool grease (lanolin), 20 percent suint (principally potash salts from sweat), 20 percent inert dirt, and 10 percent vegetable matter. The impurities are easily dissolved in water, except for the grease. Thus, the pollution load from the scouring process is extremely high in BOD and grease, has a turbid brown color due to the large amounts of dirt and grease, has a generally high alkalinity, and a temperature between 115°F and 125°F. In an average plant, 50 to 60 pounds of chemicals (detergents, alkali, softeners, etc.) are used for each 1,000 pounds of scoured wool. The total wasteload is, therefore, composed of 1,000 pounds of grease, suint, and dirt plus 50 to 60 pounds of chemicals; or 1,050 to 1,060 pounds of total solids for each 1,000 pounds of scoured wool output.

Costs of treating this effluent by chemical means is relatively high and treatment by biological means is not feasible without pretreatment for grease removal. Chemical or mechanical methods can be used to remove grease. However, the process is an economical burden due to the lack of a market for recovered grease.

Solvent scouring is a technically feasible method of grease removal. In the solvent scouring method, the grease is removed in the solvent distillery and the spent solvent is distilled and reused. However, the lack of a market for grease creates a financial bias against this process.

Dyeing produces an acid waste which is highly colored and relatively high in BOD. It may also be slightly toxic depending on the type of dye used.

Wastes from the wash after fulling contain a high concentration of BOD and oil. In addition, these wastes have temperatures ranging from 110°F to 150°F.

Table A-3-2 lists the substances found in the liquid waste from a typical finishing mill for wool textiles. The waste analysis given is for a combination of all the liquid wastes from all processes in the mill including scouring, dyeing, and washing.

Table A-3-2
Process Chemical Inventory and BOD Survey—Woolen Mill

Process Chemical	Chemical Composition and Use	% OWF* Used			Conc'n in Effluent	BOD	
		Scouring and Carding	Finishing	Total		% OWC*	% OWF*
Soap	Fatty acid soap; scouring, fulling	2.1	5.5	7.6	152	155	11.7
Soda Ash	Na_2CO_3; scouring, fulling	14.2	2.8	17.0	340	0	0
Quadrafos	$Na_6P_4O_{13}$; washing	0.5	0	0.5	10	0	0
Pine Oil	Pine Oil, washing	0.5	0	0.5	10	108	0.5
Paragon 500		0.5	0	0.5	10	—	—
Prozol T	Mineral oil plus nonionic emulsifier; carding	0.5	0	0.5	10	20	0.1
Acetic acid 84%	CH_3COOH; dyeing		1.2	1.2	24	62	0.7
Olive Sub C3 —	Oil; spinning	0.4	0	0.4	8		
Sulfuric acid —	H_2SO_4; carbonizing, dyeing	0	0.2	0.2	4	0	0
Chrome mordant —	$NA_2CR_2O_7 + (NH_4)_2SO_4$; dyeing	0	0.4	0.4	8	0	0
Chrome	$Na_2Cr_3O_7$; dyeing	0	0.6	0.6	12	0	0
Glauber salt —	Na_2SO_4; dyeing	0	0.4	0.4	8	0	0
Monochlorobenzene	C_6H_5Cl; dyeing	0	0.2	0.2	4	3	0
Nopco 1656	Soluble fatty ester; spinning	0	0.2	0.2	4	12	0
Iversol	Blend of soaps, solvents, and detergents; washing	0	1.6	1.6	32	60	1.0
Rinsol	Detergent; washing	0	2.9	2.9	58	72	2.1
Supertex E	Fatty acid soaps, solvent, cresylic acid; washing	0	0.2	0.2	4	25	0.1
Wool Finish B	High carbohydrates and enzymes; finish	0	2.3	2.3	46	57	1.3
	Sub-total	18.7	18.5	37.2	748		17.5
	Natural Impurities						
	Grease, suint, dirt	150.0	0	150.0	3000	16.7	25.0
	Grand Total	168.7	18.5	187.2	3748		42.5

* % OWC is BOD inherent in chemical, based on its weight.
% OWF is BOD due to the chemical, based on weight of wool.

(2) Cotton Industry

1. Production Processes

Raw cotton is converted to woven cloth or yarn before any finishing processes are performed. The fundamental processes for converting raw cotton to finished textile goods are as follows:

- Conversion to cloth
- Desizing
- Scouring or boil-off
- Bleaching
- Mercerizing or causticizing
- Dyeing
- Printing
- Finishing.

Conversion to cloth and yarn is usually achieved in a weaving mill, but this process does not directly produce any hazardous wastes and is not included in the SIC codes under consideration. Thus, the wastes from this process will not be discussed in detail in this section.

2. Waste Characteristics

The major sources of pollutants in a cotton finishing plant are the desizing, scouring, and dyeing operations. Wasteloads from other operations are less significant in strength and volume.

The subprocess wastes which are most likely to cause difficulty in treatment come from desizing and dyeing, due to their high concentrations of BOD chemicals and solids. The BOD chemicals exert an oxygen demand on the receiving watercourse and may kill fish, produce taste and odor, form floating scum, and generally be detrimental to beneficial uses of the watercourse. Dyehouse wastes add aesthetically objectionable color to the watercourse and, in addition, may be toxic and either acidic or basic.

Chemical pollutants normally consist of acids, alkalis, and inorganic salts. They may kill aquatic life, produce taste and odor, inhibit municipal waste treatment processes, and render the watercourse unfit for agricultural, municipal, and industrial uses.

Cotton finishing mills also present waste treatment problems because wastes from the same plant vary greatly at different times, especially dyehouse wastes. This presents a problem because biological waste treatment processes often do not operate efficiently when subjected to wastewater influents that vary widely in chemical constituents from day to day.

In cases where the waste discharge from the plant is a significant portion of the water flowing in the watercourse, thermal pollution will result. A temperature rise in the receiving water may prove detrimental to beneficial uses downstream.

Table A-3-3 lists the substances found in the liquid waste from a typical finishing mill for cotton textiles. The waste analysis given is for a combination of all the liquid wastes from all processes in the mill, including desizing, scouring, and dyeing.

Table A-3-3
Process Chemical Inventory and BOD Survey—Cotton Plant*

Chemical	Pounds Used	BOD**			Effluent Concentration	
		% OWC	Pounds	% of Total	p.p.m.	B.O.D.
		Desize Contribution				
Slashing Starch (glucose)	733134	59	432549	69.5	176.0	103.8
Sub-total	733134	—	432539	69.5	176.0	103.8
		Scour(Kier) Contribution				
Natural Impurities	337800	—	128364	20.6	81.1	30.8
Sub-total	337800	—	128364	20.6	81.1	30.8
		Process Chemical B O D. Contribution				
Soap	13715	140	19125	3.7	3.3	4.6
Acetic Acid 56%	54350	35	19023	3.6	13.1	4.2
Sodium hydrosulfite	113250	11	12458	2.0	27.2	1.5
Urea	85600	9	7704	1.2	20.5	1.8
Rhozyme LA	45600	2	912	0.1	10.9	0.2
Tergitol NPX	63000	2	1260	0.2	15.1	0.3
Detergent MPX	11700	8	936	0.1	2.8	<0.1
Sub-total	387215		61418	9.9	91.9	12.6
	Process Chemicals with Negligible B O D Contributions					
Caustic Soda (100%)	2148000				513.8	
Sodium bicarbonate	260300				62.5	
Sodium hypochlorite	236100				56.6	
Sodium chloride	144800				34.7	
Sulfuric acid	137600				32.2	
Sodium silicate	67500				16.0	
Sodium carbonate	56000				13.8	
Phosphoric acid	44100				10.6	
Hydrogen peroxide (30%)	27500				6.6	
Sodium chlorite	23000				5.5	
Sub total	3144900				752.3	
Grand Total	4603049		622331		1102.2	147.2

* This plant received 6,431,000 pounds of goods during the inventory period (1 year) and used 2,000,000 gallons of water per day. It desized all of the cloth but caustic boiled only 3,378,000 pounds of it. The remaining "fancy" cloth, with colored pattern already woven in, (3,053,000 pounds) was peroxide kiered. The plant dyed 2,360,000 pounds and left 1,018,000 pounds white.

** % OWC is B O D inherent in the chemical based on its own weight. Pounds equals the pounds of B O D exerted by the chemical. % of the total is the % contributed by the chemical to the total plant B O D

(3) Synthetic Fiber Industry

1. Production Processes

Synthetic fibers fall into two main groups; they are those produced from cellulose and those produced synthetically from organic materials. The cellulose fibers are principally rayon and acetate. The organic fibers are principally acrylics, polyesters, and nylon.

The funadamental processes for finishing rayon and acetate fabrics are as follows:

- Chemical preparation
- Scouring and dyeing
- Salt bath (rayon only)
- Special finishing (optional).

The fundamental processes for finishing nylon, acrylic, and polyester fabrics usually are as follows:

- Scouring
- Dyeing or bleaching
- Scouring (acrylic and polyester only)
- Special finishing (optional).

2. Waste Characteristics

The three key waste-producing steps in the series of finishing processes for synthetic textiles are scouring, dyeing or bleaching, and special finishing.

Dyeing of polyester and acrylic fabrics presents a particularly difficult waste problem due to the odors, toxic vapors, and high BOD of the carriers, and the heat of the waste water. Use of pressure dyeing is increasing as machinery such as Burlington's Hy Press dye machine comes into use. Where carriers continue to be used, monochlorobenzene has the advantage of very low BOD in comparison to other carriers. It has the disadvantage of requiring venting facilities due to its toxic fumes.

Table A-3-4 lists the substances found in the liquid waste from the various subprocesses making up the finishing process for the different types of synthetic fibers.

4. WASTE DISPOSAL PROCESSES AND PRACTICES

There are two fundamental principles which may be followed in order to reduce or eliminate the potential hazards presented to the

Table A-3-4
BOD Contribution of Process Chemicals Used in Finishing of Synthetic Fibers

Fiber	Process	Process Chemical	BOD		ppm
			% OWC	% OWF	
Rayon	Chemical Preparation	Antistatic lubricants, oil, dye, synthetic detergent			
	Scour	Synthetic detergent	14	0.4	
		Antistatic lubricants	--	1.5	
		Oil	53	1.1	
	Scour and Bleach	Synthetic detergent, H_2O_2			
	Salt Bath	Synthetic detergent, sodium chloride, sulfates			
Acetate	Chemical Preparation	Antistatic lubricants, soap, tetrosodium pyrophosphate, soda, fatty esters			
	Scour and Dye	Antistatic lubricants	--	1.5	
		Sulfonated oils	52	1.0	
		Esters	41	0.8	
	Scour and Bleach	Synthetic detergent, H_2O_2 or chlorine			
Nylon	Scour	Antistatic lubricants	--	1.5	612
		Soap	150	1.5	612
		Tetrasodium pyrophosphate, soda			
		Fatty esters	55	0.6	204
	Developed Dispersed Dye	Dye, $NaNO_2$, HCl, developer, sulfonated oils	56	1.7	
	Bleach	Peracetic acid			

Table A-3-4

Continued

Fiber	Process	Process Chemical	BOD		ppm
			% OWC	% OWF	
Acrylic	Cuprous Ion, Phenol Dye	Dye, formic acid	20	0.6	
		Wetting agent	14	0.1	
		Phenol	200	6.0	
		Aromatic amines, glyoxal, sulfates	4	0.1	
	Thermosol Padding Dye	Acid			
	Bleach	Chlorite			
	Scour	Synthetic detergent	0	0	
		Pine oil	108	1.1	
Polyester	Scour	Antistatic lubricants	--	1.5	
		Chlorite, hypochlorites, non-ionic synthetic detergent	5	0.1	
	Thermosol Padding	Acid			
	Dye With Carrier	Dye			
		Monochlorobenzene or orthochlorobenzene			$<$480
		or phenylmethyl carbinol	150	45.0	19,000
		or salicylic acid	141	56.4	25,000
		or benzoic acid	165	66.0	25,000
		or orthophenylphenol	138	13.8	6,060
	High Temperature & Pressure Dye	Dye			
	Bleach	Chlorite, NaNO$_2$, acetic acid, oxalic acid, nitric acid, bisulfates, proprietary bleaches			

public health and welfare by waste materials and effluents from industry.

- Improve production subprocess design by:
    - Reducing the amount of waste from a subprocess
    - Recycling the waste from a subprocess to the same or other subprocesses
    - Requiring different process compounds less hazardous than previous compounds when appearing in the waste stream
    - Developing new subprocesses which would require less hazardous compounds
    - Developing useful purposes for waste materials.
- Improve waste treatment capability by:
    - Construction of new facilities or enlargement of present facilities to ensure that all wastes are treated
    - Installation of new techniques to increase efficiency in present facilities so that increased wasteloads can be effectively treated
    - Installation of new techniques to increase the effectiveness of present facilities so that treated wastes pose a lesser hazard to the public health and welfare.

The following paragraphs describe how these two principles have been applied to the finishing process industries for the three major types of textiles and the degree to which they have been applied.

(1) Wool Industry

1. Production Subprocesses

Table A-3-5 shows the subprocess trends since 1950 and projects them to 1982. Of course, most subprocess changes are initiated and developed for reasons other than pollution reduction. However, certain subprocesses do afford a reduction in waste production when compared to 1950 technology subprocesses. These waste reduction figures expressed as a percentage of the wastes generated in 1950 are presented in Table A-3-6.

By-product utilization depends on economic considerations. It is estimated that 50,000 to 100,000 tons of wool grease and 20,000 to 40,000 tons of suint could be utilized if the market for these products made it economically feasible. Lanolin is recovered from the wool grease and potash from the suint.

The amount of process water reused in 1964 was considerably greater than in 1950 when older methods were practiced. Counter-current scouring can reduce the amount of water required by as much as 6,000 gallons/1,000 pounds

Table A-3-5
Wool Industry Subprocess Trends

Production Process and Significant Subprocesses	Estimated Percentage of Plants Employing Process in:				
	1950	1963	1967	1972	1982
Scouring					
Soap/alkali	80	0	0	0	0
Syndet	0	80	50	40	30
Non-ionic syndet	0	0	40	50	65
Solvent	20	20	10	10	5
Dyeing					
Sodium Sulfate	100	100	100	100	100
Sulfur Dioxide	40	10	5	0	0
Hydrogen Peroxide	40	70	75	85	95
Acetic Acid	20	20	20	15	5
Sulfuric Acid	100	100	100	100	100
Carding					
Olive Oil	20	0	0	0	0
Synthetic Oil*	80	100	100	100	100
Fulling					
Soap	95	10	0	0	0
Synthetic Chemicals	0	70	80	90	100
Sulfuric Acid	5	20	20	20	0
Washing					
Soap	100	0	0	0	0
Syndet	0	100	100	100	100
Carbonizing					
Sulfuric Acid	100	100	100	100	100

---

* 20 percent BOD content by weight.

Table A-3-6
Process Pollution Reduction

Process and Subprocesses	BOD lb/ 1000 lb	Waste Reduction Effectiveness (%)	Remarks
Scouring			
Soap/Alkali	250	0	
Syndet	221	11.6	Syndet denotes Synthetic Detergent
Solvents	10	96	
Dyeing			
Acetic Acid	49	30	
Ammonium Sulfate	10	86	
Sulfuric Acid	70	0	
Washing			
Soap/Alkali	150	0	
Syndet	64	57.3	20 percent BOD oil used for carding
Syndet	30	80	BOD reduction due to use of 3 percent BOD oil in carding
Carbonizing			
Sulfuric Acid plus Sodium Carbonate	2	0	

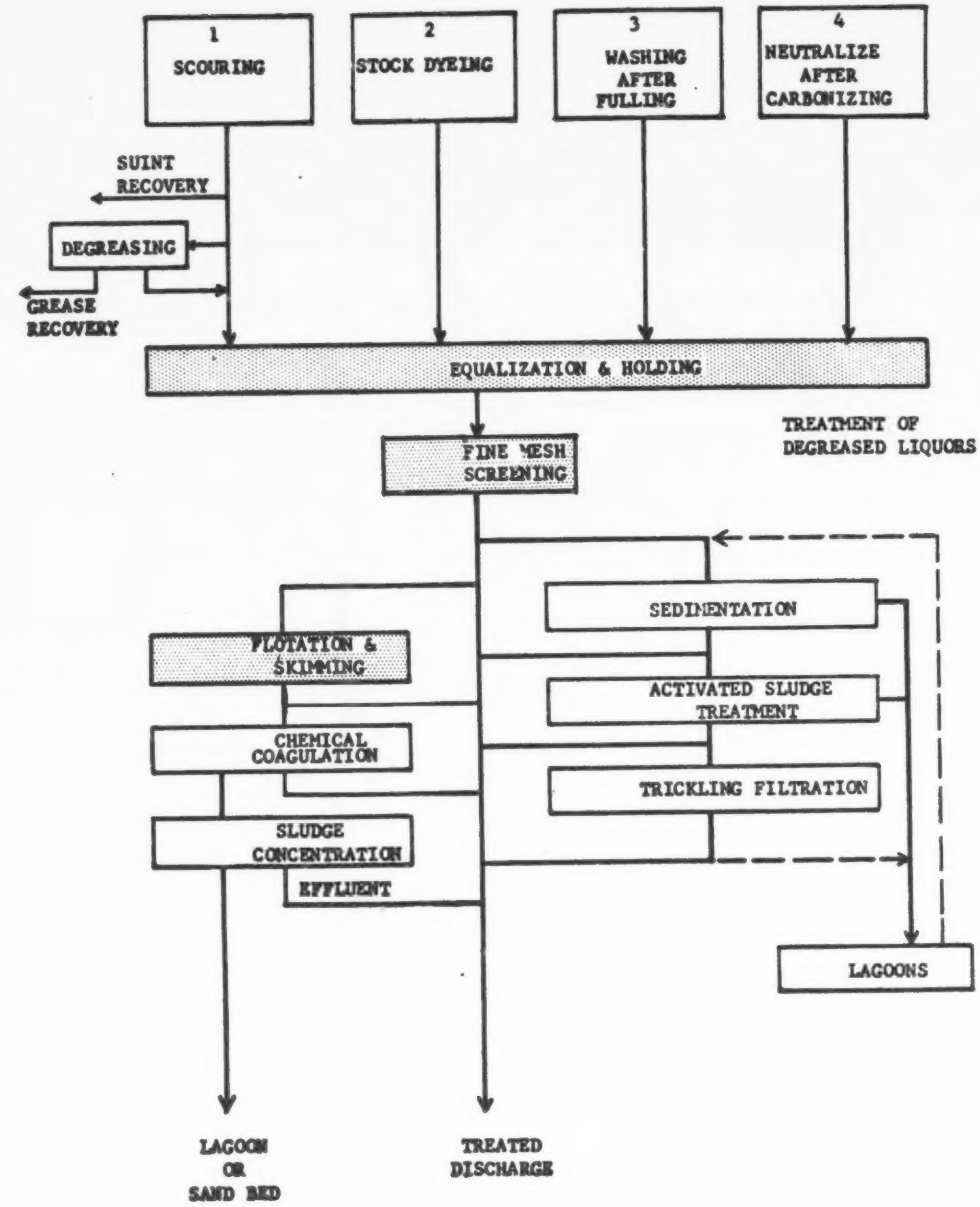
of wool. Reuse of rinse waters in the wash after fulling can reduce water requirement by approximately 4,000 gallons/1,000 pounds of wool. It has been estimated that, in 1964, the wool industry as a whole reused approximately 5 percent of its process water and 95 percent was used only once.

2. Waste Treatment Capability

Figure A-3-2 is a waste treatment flow chart for the wool textile finishing industry. The four main subprocesses involved in wool finishing are depicted, and the possible treatments for each waste are shown. Treatment practices vary from finishing mill to finishing mill, so that any treatment process or combinations of processes may prevail at a given wool finishing mill.

The most common practices of waste treatment in the wool industry are biological methods, such as sedimentation, activated sludge, trickling filtration, and lagooning. Screening is almost universally used to remove fibers which may possibly damage subsequent treatment facilities. Equalization and holding are generally necessary

FIGURE A-3-2
Wool Textile Production Waste Treatment Flow Chart-SIC 2231


1
SCOURING
2
STOCK DYEING
3
WASHING AFTER FULLING
4
NEUTRALIZE AFTER CARBONIZING
SUINT RECOVERY
DEGREASING
GREASE RECOVERY
EQUALIZATION & HOLDING
TREATMENT OF DEGREASED LIQUORS
FINE MESH SCREENING
SEDIMENTATION
FLOTATION & SKIMMING
ACTIVATED SLUDGE TREATMENT
CHEMICAL COAGULATION
TRICKLING FILTRATION
SLUDGE CONCENTRATION
EFFLUENT
LAGOONS
LAGOON OR SAND BED
TREATED DISCHARGE

due to batch dumping of many of the process wastes creating shock loads and intermittent flows through the treatment system.

In the past, wool wastes were treated by chemical precipitation without pretreatment for grease recovery; however, the present trend is toward biological oxidation and chemical pretreatment due to economic factors. Work in recent years by Souther and others indicates clearly that the activated sludge process with modifications (primarily extended aeration time and influent pH adjustment) will consistently produce BOD reductions on the order of 90 percent. As the discharge requirements imposed upon the textile finishing plants are upgraded, it is probable that future waste treatment facilities will be predominantly of the activated sludge type.

The percentage of wool finishing wastes treated by municipal plants is also increasing steadily as costs of building and maintaining inplant treatment facilities increase. Newer finishing mills are being built close to municipalities rather than in rural areas to take advantage of the availability of municipal treatment.

Much of this industry's waste is discharged to municipal sewers because they are often located adjacent to or within population centers. Industry wastes are generally pretreated by grease removal techniques and screening prior to discharge into a municipal system. Municipal waste treatment plants are not equipped to easily handle the large amounts of grease produced by wool mills. Screening for removal of fibers is also necessary to prevent clogging of biological treatment equipment and to reduce the quantity of suspended matter. Carrying rates of waste production require holding tanks and surge basins to minimize peak discharge and provide for more or less uniform rates of release to sewers. Municipal treatment without pretreatment may be feasible in the case of high capacity chemical coagulation treatment plants.

Table A-3-7 shows the effectiveness of the various treatment processes in removing selected pollutants.

Table A-3-8 provides some historical data and some projections as to the percentage of wool finishing mill wastes being treated by municipal facilities, industrial facilities, and that percentage which is not being treated.

Table A-3-7
Treatment Removal Efficiencies

Treatment Method	Normal Reduction Percent				
	BOD	Grease	Color	Alkalinity	SS
Grease Recovery					
Acid Cracking	20-30	40-50	0	0	0-50
Centrifuge	20-30	24-45	0	0	40-50
Evaporation	95	95	0	0	
Screening	0-10	0	0	0	20
Sedimentation	30-50	80-90	10-50	10-20	50-65
Flotation	30-50	95-98	10-20	10-20	50-65
Chem. Coagulation					
$CaCl_2$	40-70				80-95
Lime + $CaCl_2$	60	97			80-95
CO_2 - $CaCl_2$	15-25				80-95
Alum	20-56*		75		
Copperas	20*				
H_2SO_4+ Alum	21-83*				
Urea + Alum	32-65*				
H_2SO_4+ $FeCl_2$	59-84*				
$FeSO_4$	50-80				
Activated Sludge	85-90	0-15	10-30	10-30	90-95
Trickling Filtration	80-85	0-10	10-30	10-30	90-95
Lagoons	0-85	0-10	10-30	10-20	30-70

Table A-3-8
Projected Net Wasteloads

Year	Gross Waste Generated BOD million lb	Waste Treated Municipally percent	Average Reduc-tion percent	Waste Treated By Industry percent	Average Reduc-tion percent	Untreated Wastes percent	Total Reduction percent	Net Waste Discharged BOD million lb
1963	132	38.5	85	21.0	70	40.5	47.4	69.4
1967	132.5	40.0	86	23.0	71	37.0	50.7	65.4
1968	132.8	40.5	86	23.5	71	36.0	51.5	64.5
1969	132.9	41.0	86	24.0	71	31.0	52.4	63.3
1970	133.0	41.5	87	24.5	72	34.0	53.7	61.6
1971	133.1	42.0	87	25.0	72	33.0	54.6	60.4
1972	133.2	42.5	87	25.5	73	32.0	55.4	59.4
1977	134.2	45.0	88.5	28.0	74	27.0	60.6	52.9
1982	136	48.0	90	31.0	76	21.0	66.8	45.1

(2) Cotton Industry

1. Production Subprocesses

Table A-3-9 shows the subprocess trends in the cotton finishing industry since 1950 and projects them to 1982. It should be pointed out that which subprocess is used depends upon such factors as type and color of cotton cloth being finished, type and size of process machinery available, skill of available operating personnel, and length of run.

Table A-3-10 indicates the potential pollution reduction by substitution of alternate manufacturing subprocesses. In most cases, the reduction is associated with high-speed continuous machines or substitution of alternate chemicals. The economic feasibility of purchasing new machinery or substituting alternate chemicals is, of course, an individual decision for each finishing plant. It is anticipated that pollution reduction will become an increasingly important factor in future management decisions.

Table A-3-9
Subprocess Trends

Fundamental Process and Subprocesses	% of Plants Employing Subprocess				
	1950	1963	1967	1972	1982
Desizing					
Enzyme	80	58	15	5	0
High T° Enzyme	20	40	80	85	85
Water (used with CMC)	0	2	5	10	15
Scouring					
Boil-Off	15	15	15	10	5
Kier Boil	70	50	20	5	0
Cont. Scouring	-	20	50	75	90
Wet Out	15	15	15	10	5
Bleaching					
Hypochlorite	50	20	20	10	0
Hydrogen Peroxide	50	80	80	90	100
Continuous	-	50	60	70	80
Mercerizing and Causticizing					
NaOH	40	35	30	25	20
Dyeing					
Vat	90	90	90	90	80
Basic	10	5	0	0	0
Direct	70	75	80	80	90
Naphthol	60	55	50	45	35
Developed	70	50	30	10	0
Sulfur	90	90	90	85	75
Aniline Black	5	5	5	5	5
Fiber Reactive	10	20	40	50	70
Printing					
Roller	95	95	95	90	90
Screen	4	4	4	0	0
Other	1	1	1	10	10

Table A-3-10
Pollution Reduction by Alternate Subprocesses

Fundamental Processes and Subprocess	BOD Lb/1000 Lb	Process Reduction Efficiency (%)	Remarks
Desizing:			
Enzymes	67	0	BOD Reduction due mainly to use of CMC/Starch Formulation in weaving mill.
Water CMC/ Starch Formulation	20	70	
Scouring:			
Boil-off	53	0	NaOH used in both cases but cont. process allows use of less solution.
Contin. Scour	42	21	
Bleaching:			
Bins	4	0	H_2O_2 used predominantly
Continuous	3	25	
Mercerizing and Causticizing			
Continuous	15	0	
Cont. in Recovery of NaOH	6	60	
Dyeing:			
Batch	10 - 60	0	Synthetic detergents used in wash after dyeing.
Continuous	5 - 32	50	
Syn. Det.	5 - 8	80	
Printing:			
Roller w/soap wash	43	0	In Prevalent tech., both soap and synthetic detergents are used.
Roller with Syndet wash	19	53	
Soap & Syndet	30	30	

These waste reduction figures are expressed as a percentage of the waste generated by a particular subprocess using 1950 technology. The values shown are generally the highest reductions for a particular alternate subprocess.

There is no significant by-product use of wastes in the cotton textile finishing industry. Various researchers have attempted to develop economically feasible methods for recovery of the expensive dyeing compounds, but were unsuccessful. No future by-product use on a significant scale is predicted.

It is estimated that approximately 16 percent of the industry process water is reused, and 84 percent is used only once. It appears that the percentage of process water reused will increase in the future because newer machinery is often of continuous or counter-current design. In addition, because process water is becoming more expensive in many areas, there will be increased use of instrumentation to control processes more precisely.

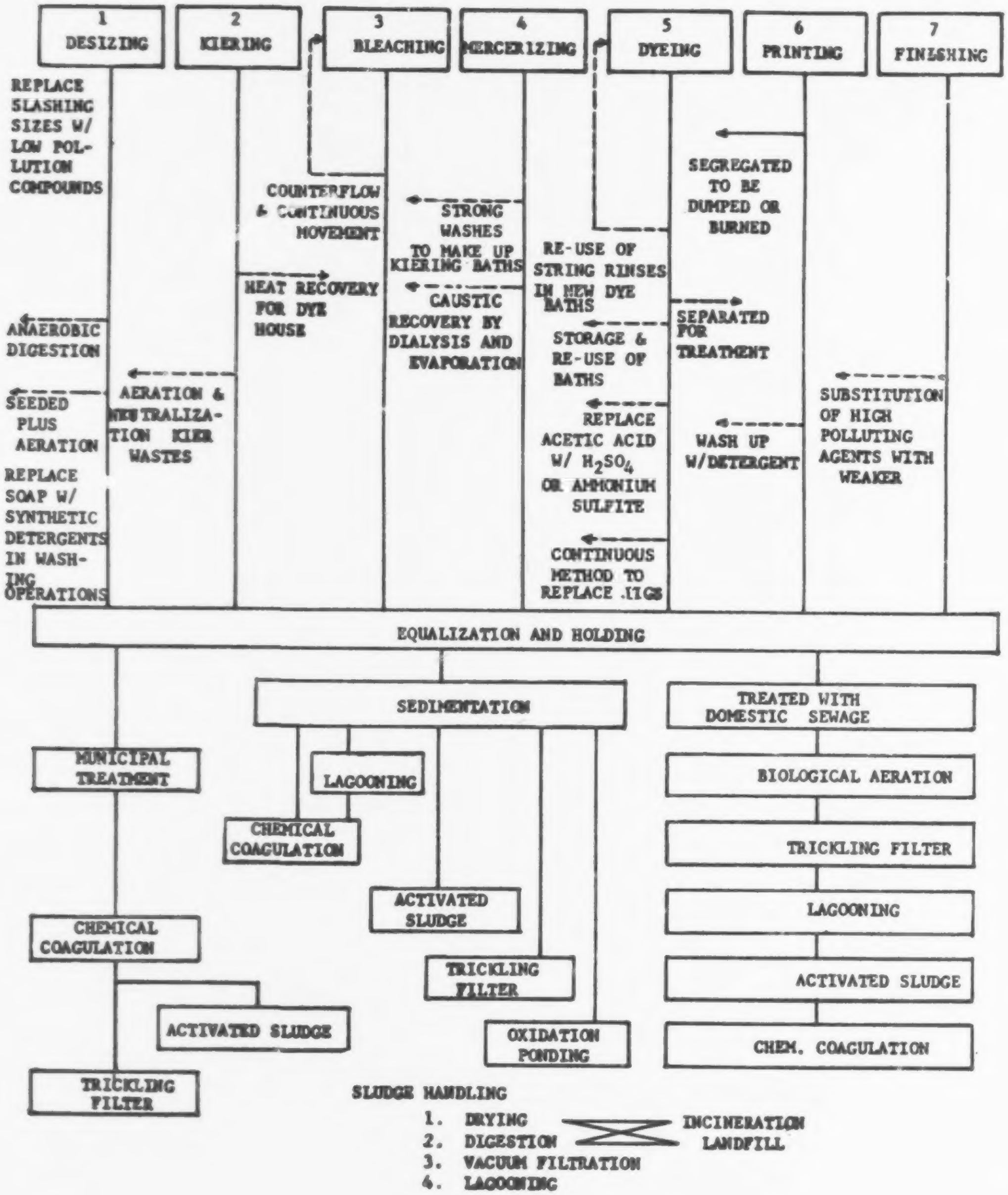
2. Waste Treatment Capability

Figure A-3-3 is a waste treatment flow chart for the cotton textile finishing industry. Seven principal subprocesses involved in cotton finishing are depicted, and the possible treatments for each waste are shown. Treatment practices vary from finishing mill to finishing mill so that almost any treatment process or combination of processes may prevail at a given cotton finishing mill.

Generally, the textile cotton finishing waste treatment process should begin with a holding and equalization basin. This will level out the volume of flow and pollution strength to the following treatment units. A reasonably uniform waste can be treated biologically with much greater success than can a widely fluctuating waste.

Since the waste is relatively low in suspended solids and high in dissolved solids, it is often feasible to skip the primary settling step and begin directly with the aeration tank. In some cases where the pH is too high, toxic elements or some other factors inhibiting to the biological treatment may be present, making chemical pretreatment necessary prior to the aeration tank.

FIGURE A-3-3
Cotton Textile Finishing Waste
Treatment Flow Chart-SIC 2261


1 DESIZING
2 KIERING
3 BLEACHING
4 MERCERIZING
5 DYEING
6 PRINTING
7 FINISHING
REPLACE SLASHING SIZES W/ LOW POLLUTION COMPOUNDS
COUNTERFLOW & CONTINUOUS MOVEMENT
STRONG WASHES TO MAKE UP KIERING BATHS
RE-USE OF STRING RINSES IN NEW DYE BATHS
SEGREGATED TO BE DUMPED OR BURNED
HEAT RECOVERY FOR DYE HOUSE
CAUSTIC RECOVERY BY DIALYSIS AND EVAPORATION
SEPARATED FOR TREATMENT
STORAGE & RE-USE OF BATHS
ANAEROBIC DIGESTION
AERATION & NEUTRALIZATION KIER WASTES
SEEDED PLUS AERATION
REPLACE ACETIC ACID W/ H_2SO_4 OR AMMONIUM SULFITE
WASH UP W/DETERGENT
SUBSTITUTION OF HIGH POLLUTING AGENTS WITH WEAKER
REPLACE SOAP W/ SYNTHETIC DETERGENTS IN WASHING OPERATIONS
CONTINUOUS METHOD TO REPLACE JIGS
EQUALIZATION AND HOLDING
SEDIMENTATION
TREATED WITH DOMESTIC SEWAGE
MUNICIPAL TREATMENT
LAGOONING
BIOLOGICAL AERATION
CHEMICAL COAGULATION
TRICKLING FILTER
ACTIVATED SLUDGE
LAGOONING
CHEMICAL COAGULATION
TRICKLING FILTER
ACTIVATED SLUDGE
ACTIVATED SLUDGE
OXIDATION PONDING
CHEM. COAGULATION
TRICKLING FILTER
SLUDGE HANDLING
1. DRYING
2. DIGESTION
3. VACUUM FILTRATION
4. LAGOONING
INCINERATION
LANDFILL

The activated sludge process for cotton textile waste is often modified by increasing the aeration time and carrying a higher concentration of mixed liquor suspended solids in the aeration tank. With careful operation, this process will produce excellent reduction of BOD and suspended solids. If some domestic sewage is available to mix with the textile waste, the efficiency of the plant is generally increased.

To lower construction costs, an aerated lagoon is sometimes substituted for the activated sludge process. Properly operated, it is capable of closely approaching the pollution removal efficiency of the conventional activated sludge process.

The trickling filter biological treatment is widely installed, but the trend is away from its use in recent years. It cannot reach the removal efficiencies of the activated sludge process and generally lacks operational flexibility.

Where cheap land is available, an inexpensive tertiary treatment is simple storage in a pond of the secondary effluent from the biological treatment process. Simple storage will often reduce the effluent pollution load an additional 50 percent, for example, increasing removal from 90 to 95 percent.

It is estimated, however, that by 1972, 40 percent of cotton textile finishing mill wastes will be discharged into municipal sewer systems. Many municipal waste treatment methods will be susceptible to shock loads from the mills; therefore, pretreatment should include flow regulation and equalization holding procedures to ensure waste uniformity. In a large municipality, the mill waste would be diluted sufficiently before reaching the treatment facility and would not harm the operation. Even so, most large municipalities require finishing plants to provide screening and constant discharge holding basins. Normally, a cotton finishing plant waste is easily handled by conventional treatment methods.

Table A-3-11 shows the effectiveness of the various treatment processes in removing selected pollutants. Based on a typical waste generated by prevalent plants in the base year, 1963, the removal efficiencies are expressed in terms of percentage of gross wasteload removed by the removal process. It is assumed that the auxiliary units normally associated with the removal method are included.

Table A-3-11
Treatment Removal Efficiencies

Removal Method	Removal Efficiency (Percent)		
	BOD	SS	TDS
Screening	0-5	5-20	0
Plain Sedimentation	5-15	15-60	0
Chemical Precipitation	25-60	30-90	0-50
Trickling Filter	40-85	80-90	0-30
Activated Sludge	70-95	85-95	0-40
Lagoon	30-80	30-80	0-40
Aerated Lagoon	50-95	50-95	0-40

Table A-3-12
Waste Treatment Projections

Year	Percent Waste Treated Municipally	Average Reduction (Percent)	Percent Waste Treated By Industry	Average Reduction (Percent)	Total Reduction (Percent)
1967	35	85	25	80	49.5
1968	36	85	27	80	52.0
1969	37	85	29	80	54.5
1970	38	86	31	80	57.5
1971	39	86	33	80	60.0
1972	40	86	35	80	62.5
1977	43	87	40	80	69.5
1982	45	87	45	80	75.0

For example, the removal efficiencies for the activated sludge process and trickling filter process assume that the primary and secondary sedimentation tanks are included in the process.

Table A-3-12 provides some projections as to the percentage of cotton finishing mill wastes treated by municipal facilities and that percentage treated by industrial facilities. The average percent of waste reduction for these two types of treatment is also projected, and this affords a prediction of the percentage of total waste reduction.

The rate of adoption of waste treatment practices in the textile finishing industry has paralleled, to some extent, the trends in the municipal sewage treatment area. As technology has advanced, the attainable standards of pollution reduction have increased also.

Work in recent years by Souther and others indicates clearly that the activated sludge process with modifications (primarily extended aeration time and influent pH adjustment) will consistently produce BOD reductions on the order of 90 percent. As the discharge requirements imposed upon the textile finishing plants are upgraded, it is probable that future waste treatment facilities will be predominantly of the activated sludge type.

The rapid increase in treatment predicted in Table A-3-12 is based on continued strong pressure by regulatory agencies upon industry to reduce pollution discharged, continued large capital investment to build new plants and phase out old ones, continued tendency to locate new plants where a municipal sewer is available for waste discharge, and advancing technology in waste treatment processes.

(3) Synthetic Fibers Industry

1. Production Subprocesses

Table A-3-13 shows the subprocess trends in the synthetic textile finishing industry since 1963 and projects them to 1982. It should be pointed out that there are often alternate methods to accomplish a particular operation in the synthetic textile finishing process. Which method is used depends upon such factors as type and color of cloth being finished, type and size of process machinery

Table A-3-13
Subprocess Trends

Textiles and Processes	Estimated Percentage of Plants Employing Process				
	1950	1963	1967	1972	1982
Chemical Preparation rayon & acetate					
1. Scour		100	100	100	100
Scour: nylon, acrylic, polyester					
1. Soda Ash		10	5	5	2
2. Caustic Soda		10	15	20	20
3. Ammonium Hydroxide		60	65	70	70
4. Sodium Carboxymethyl Cellulose		50	60	70	70
Scour and Dye: rayon					
1. Direct		100	100	100	100
2. Naphthol		30	30	20	20
3. Developed		40	50	60	65
4. Vat		60	60	70	70
Scour and Bleach: rayon & acetate					
1. Hydrogen Peroxide		50	55	60	65
2. Hypochlorite		50	45	40	35
3. Sodium Chlorite		80	70	60	50
Dye Nylon:					
1. Dispersed		60	60	70	70
2. Acid		20	20	10	10
3. Direct		20	20	20	20
Dye Acrylic:					
1. Cationic w/cationic retarder		50	45	40	30
2. Cationic w/anionic retarder		10	10	5	5
3. Disperse		60	70	80	90
4. Basic		60	70	80	90
Dye Polyester:					
1. Conventional		5	5	5	-
2. w/Orthophenylphenol		3	20	20	20
3. w/Chlorinated benzenes		2	10	15	25
4. Benzoic or Salicylic Acid		40	20	10	-
5. Phenylmethyl carbinol		40	20	10	-
6. High Temp. & Pressure		5	15	25	35
7. Thermosol Padding		5	10	15	20

Table A-3-13
Continued

Textiles and Processes	Estimated Percentage of Plants Employing Process				
	1950	1963	1967	1972	1982
Bleach: nylon, acrylic, polyester					
1. Sodium Chlorite		30	20	10	10
2. Peracetic Acid		50	50	50	40
3. Hydrogen Peroxide & Sodium Hypochlorite		20	30	40	50
Final Scour: acrylic & polyester					
1. Soda Ash		10	5	2	2
2. Caustic Soda		10	10	20	30
3. Ammonium Hydroxide		70	70	80	85
4. Sodium Carboxymethyl Cellulose		30	40	50	60
Heat Set: all fibers					
1. Optional		80	85	90	95
Finishing: all fibers					
1. Optional		70	75	80	95

available, skill of available operating personnel, length of run, and other factors. The primary considerations in choosing one method over another are production efficiency and product quality, and any decrease in wasteload produced by the operation is merely a bonus.

Table A-3-14 outlines the relative pollution reduction potentials of the various alternative subprocesses used in the synthetic textile industry. The "older" technological method in each case is used as the basis for comparison. The values shown are generally the highest reported reductions for a particular alternate subprocess.

The thermosol dyeing process is an example in that it produces little liquid waste. Some special finishing processes use padding to apply the finish and therefore produce little waste.

There would be an adequate market for wastes reclaimed in synthetic fiber finishing if economically feasible methods were developed. This is due to the fact that all liquid wastes contain chemicals used in the finishing (or sizing) itself and could be reused if reclaimed.

Table A-3-14
Process Pollution Reduction

Textiles & Processes	Percent Reduction		
	Older	Prevalent	Newer
Chemical Preparation: Rayon and Acetate Lower BOD Chem.	0	2	5
Scour: Nylon, Acrylic and Polyester Continuous Scour Machine	0	10	15
Scour and Dye: Rayon and Acetate Continuous Machines	0	10	15
Scour and Bleach: Rayon and Acetate Continuous Machines	0	10	15
Dye: Nylon	0	Depends on Dye	Depends on Dye
Dye: Acrylic	0		
Dye: Polyester High temp. pressure dye machine	0	80	80
Bleach: Nylon, Acrylic, Polyester	0		
Continuous Bleaching Machine	0	5	10
Final Scour: Acrylic and Polyester Continuous Scour Machine	0	10	20
Special Finishing: All Fibers, Optional	0	Depends on Finish	

The one exception to this is the one percent OWF nylon extracted in the scour. All carriers presently recovered are reused. It is not economical to reclaim the other chemicals, such as spent developed dye bath. Thermal waste can be reused by heat transfer methods.

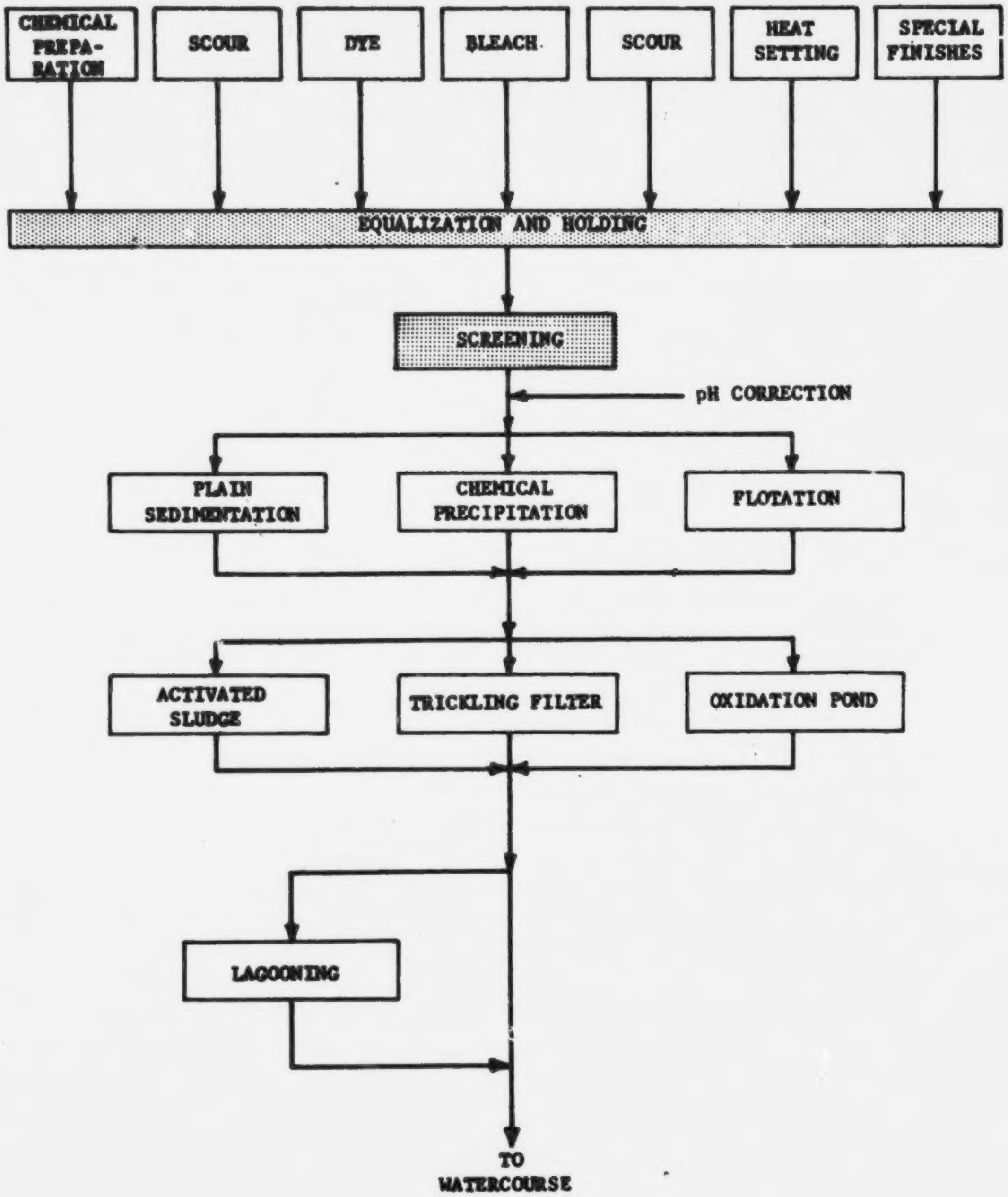
It is estimated that the synthetic textile finishing industry reused approximately 10 percent of its process water in 1964, and 90 percent was used only once.

2. Waste Treatment Capability

Figure A-3-4 is a waste treatment flow chart for the synthetic textile finishing industry. Seven principal subprocesses involved in synthetic textile finishing are depicted, and the possible treatments for the wastes from these subprocesses are shown. Treatment practices vary from finishing mill to finishing mill, so that almost any treatment process or combination of processes may prevail at a given synthetic textile finishing mill.

Synthetic textile wastes have generally been treated by biological methods with good removal efficiency at reasonable cost. In the future, it is expected that water

FIGURE A-3-4
Synthetic Textile Finishing Waste
Treatment Flow Chart-SIC 2262


CHEMICAL PREPARATION
SCOUR
DYE
BLEACH
SCOUR
HEAT SETTING
SPECIAL FINISHES
EQUALIZATION AND HOLDING
SCREENING
pH CORRECTION
PLAIN SEDIMENTATION
CHEMICAL PRECIPITATION
FLOTATION
ACTIVATED SLUDGE
TRICKLING FILTER
OXIDATION POND
LAGOONING
TO WATERCOURSE

requirements per unit production will be reduced, resulting in a plant effluent which will be higher in pollution concentration and lower in volume. Therefore, the adoption of more elaborate waste treatment facilities utilizing pretreatment and tertiary polishing can be expected.

Toxic metallic ions in dye wastes can retard biological oxidation when present in high concentrations. Chemical pretreatment may, therefore, become a requirement, or the industry may choose to adopt treatment by chemical coagulation as the principal method.

Interdependencies among processing techniques which affect wasteload removal efficiencies or cost are as follows:

- Any heavy metal ions in the waste mill normally inhibit biological treatment such as trickling filters or activated sludge. If a toxic ion is present, it may have to be removed chemically prior to further treatment or discharge.
- Toxic carriers, such as chlorinated benzenes, may inhibit bacterial growth in biological treatment. These carriers might be removed and reused because of their high cost as well as their toxic effect.

Sequences of treatment due to technical considerations are as follows:

- pH adjustment may precede other chemical treatment to reduce use of costly chemicals.
- Normally, suspended solids removal precedes biological treatment methods such as activated sludge or trickling filter, lagooning, and oxidation ponds. Certain activated sludge modifications may not require suspended solids removal.
- Sludge treatment and ultimate disposal follow sludge-producing processes, such as settling.

Substitute techniques may be:

- Biological and chemical treatments are, under certain circumstances, substitutes for each other. In other situations they may be part of the same waste treatment process.
- Sometimes fine screening may be substituted for sedimentation basins.
- Normally, the activated sludge and the trickling filter process are not used together in the same system.

Table A-3-15 shows the effectiveness of the various treatment processes in removing selected pollutants. Based on a typical waste generated by prevalent plants in the base year 1963, the removal efficiencies are expressed in terms

Table A-3-15
Treatment Removal Efficiencies

Treatment Method	Removal Efficiency (Percent)		
	BOD	SS	TDS
Screening	0 - 5	5 - 20	0
Plain Sedimentation	5 - 15	15 - 60	0
Chemical Precipitation	25 - 60	30 - 90	0 - 50
Trickling Filter	40 - 85	80 - 90	0 - 30
Activated Sludge	70 - 95	85 - 95	0 - 40
Lagoon	30 - 80	30 - 80	0 - 40
Aerated Lagoon	50 - 95	50 - 95	0 - 40

Table A-3-16
Waste Treatment Projections

Year	Municipally Treated Waste Percent	Avg BOD Reduction Percent	Industry Treated Waste Percent	Avg BOD Reduction Percent	Total Reduction Percent
1967	50	85	25	65	58
1968	51	85	26	66	60
1969	52	85	27	67	62
1970	53	86	28	68	64
1971	54	86	29	69	66
1972	55	86	30	70	68
1977	68	87	32	73	82
1982	71	88	34	76	88

of percentage of gross wasteload removed by the removal process.

Table A-3-16 provides some projections as to the percentage of synthetic textile finishing mill wastes treated by municipal facilities and the percentage treated by industrial facilities. The average percent of waste reduction for these two types of treatment is also projected, and this affords a prediction of the percentage of total waste reduction.

The tremendous growth rate of the synthetic textile industry is expected to continue and increase as various new materials (modifications of existing fibers) and new fibers are introduced to the public. Concurrent with this growth, a nearly equal increase in wasteload seems imminent. This, along with pressures by regulatory agencies regarding stream pollution, will lead to an increased rate of adoption of waste treatment practices in the future.

It is expected, however, that the gross pollution load produced by the synthetic textile finishing industry will increase significantly because of rapidly increasing production.

The organic and suspended solids pollution reaching the nation's watercourses will remain essentially constant because of a greater percentage of waste treated and higher waste treatment efficiencies. This is not true of the dissolved inorganic matter since most prevailing waste treatment methods do not significantly reduce dissolved minerals. Tertiary treatment techniques capable of removing dissolved inorganic matter are currently under extensive study, but it is unlikely that they will come into significant use prior to 1982.

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APPENDIX A-4

SIC 26—PAPER AND ALLIED PRODUCTS

1. ECONOMIC STATISTICS

This classification includes all pulp mills: those which produce only pulp, and those which produce pulp as a part of the production of either paper, paperboard, or building papers and boards. The basic financial and statistical data on the industry for 1967 is shown below (Reference 1).

SIC Code and Industry		Value of Shipments ($ Million)	Establishments Total No.	Establishments 20 or more Employees
261	- Pulp Mills	$ 730.5	61	43
262	- Paper Mills, Except Building Paper	4,844.0	354	313
263	- Paperboard Mills	2,907.0	283	264
2661	- Building Paper and Building Board Mills	341.1	94	74
	Total	$8,822.6	792	694

The 1967 geographic distribution of the industry is given by SIC code in the following table (Reference 1):

Preceding page blank

Region	261*	262	263	266
North East	15(9)	184(158)	36(36)	74(62)
North Central	11(6)	92(87)	28(28)	64(59)
South	18(12)	48(42)	27(27)	21(15)
West	17(16)	30(26)	16(16)	14(10)

* The first number indicates the total establishments; the second number (in parentheses), those with 20 or more employees.

The production of pulp and paper mill products in 1967 is shown in the following table (Reference 1):

SIC Code and Industry		Production (thousand short tons)
2611	Pulp Mills	37,066
2621	Paper Mills Except Building Paper	20,938
2631	Paperboard Mills	22,657
2661	Building Paper and Building Board Mills	2,754
		83,415

2. WASTE CHARACTERISTICS

Pulp mill operations include wood preparation, pulping, screening, washing, thickening, and bleaching. Paper mill operations include stock preparation, paper machine operation, converting, and finishing.

Wood preparation involves movement of the log from stock pile to debarking facilities. Pulping converts wood into fibers for papermaking. Four processes are currently used:

- Mechanical—Logs are forced against a grindstone in the presence of water.
- Chemigroundwood—The log is cooked before grinding.
- Sulfate (Kraft)—Alkaline solutions dissolve the lignin (non-cellulose portion of wood cementing cellulose fibers together).
- Sulfite—An aqueous solution containing metallic bisulfite (Mg, NH_3, Na) and sulphur dioxide digests the wood chips. Wastewaters generated result from spills, leaks, overflows, and cooking liquid preparation. They emanate from the same sources as in the Kraft process. This is also true for gaseous wastes.

Pulp screening separates coarse and fine fibers and removes dirt and foreign matter. Coarse screens or centrifugal cleaning is used.

Thickening (or dewatering) concentrates the screened pulp using deckers or vacuum filters. Water removed is used to thin fresh stock.

Bleaching brightens the pulp. Two-stage peroxide-hydrosulfite methods are used. After each stage of the bleaching process, a washing cycle is needed. Chlorination (followed by alkaline extraction) and oxidation bleaching are common techniques. Wastewaters are reduced by reuse of water in multistage bleaching.

In paper mills, stock preparation involves treating the pulp mechanically and chemically to form sheets. Water reusage is common with discharged wastewater contaminated by rejects and cleaners. The paper machine then converts the fiber suspension into a paper sheet. Wastewater is usually discharged into the sewer. The by-products and undesirable wastes are conveyed to an incinerator to generate power and steam. Other operations in this process include loading (addition of fillers), sizing, wet strength resins, and coloring.

Most pulp and paper mills reuse water from log plumes and debarkers, evaporators, washers, bleach plant washers, and paper machine operations.

Although modifications in fundamental operations do occur, it is not uncommon for a mill to use older technology in one process and newer technology in another.

The wastes from mill processes are high in biological oxygen demand (BOD), while production operations consume large quantities of water. Typical requirements (Reference 2) include:

Operation	Water Required (gallons/ton)	Biological Oxygen Demand (lb/ton)
Debarking and Cleaning	200 - 1,000	5 - 10
Unbleached Kraft Mill	15,000 - 40,000	50
Sulfite - Pulp	15,000 - 30,000	550 - 750
Semi-Chemical Pulp	20,000 - 30,000	100 - 200
Paper Mills	10,000 - 35,000	5 - 15
De-Inking	20,000 - 30,000	50 - 150
Jute Rope Rag	65,000 - 80,000	300 - 1,200

Water requirements can be estimated by multiplying the annual production 83,500 tons with the estimates of water requirement per ton of 20,000 - 40,000 gallons. Based on these calculations water requirements are between 1.7 and 3.4 billion gallons. These amounts compare well with the Census Bureau for 1968 of 2.2 billion gallons intake, 6.5 billion gallons total use (including recirculation) and the discharge of 2.0 billion gallons.

3. DISPOSAL PRACTICES

A wide variety of processes are available to reduce the solid, or BOD pollutants, in effluent streams. Economic considerations are paramount in effluent treatment. Processes which are inherently low cost or which can produce saleable by-products are needed to economically reduce the effluent solids with a high BOD.

The effluents from pulp and paper mills, with the exception of weak wastes and uncontaminated cooling waters, receive some form of treatment. The waste reduction practices employed are water reuse, chemical recovery, fiber and solids recovery. The major pollutants are temperature, BOD (biological oxygen demand), COD (chemical oxygen demand), color, dissolved solids, SS (suspended solids) and bacteria. At the present technological level, waste reductions of 20 to 70 percent can be obtained by water reuse (Reference 3).

Wastewater treatment practices can be divided into four groups: pretreatment, primary treatment, secondary treatment, and tertiary treatment. Other treatments may include "strong" waste digester liquor and pulp wash water handling and disposal, sludge handling and disposal, and by-product production. Wastewaters may be discharged into separate sewers according to strength and characteristics. The four major treatment processes are designed to remove as many contaminants as possible.

(1) Pretreatment

Pretreatment includes the initial operations that prepare or condition the wastewater prior to primary clarification. Wastewaters can be either combined mill effluent or segregated wastewaters.

The most common pretreatment methods used are grit and debris removal, and wastewater screening. Inorganic ash, grit from the wood preparation process, and runoff materials (sand and gravel) must be removed from the wastewaters. Gravity settling tanks, using a fixed wastewater flow velocity, remove approximately 70 to 80 percent of the grit. Bar screens are also used to remove debris.

Neutralization of mill wastewaters is also a pretreatment process. Wastewater pH can affect conditions in the receiving stream and cause possible corrosion of mechanical treatment equipments. Wastewater, after pretreatment, must have a pH of 6.5 to 8.5 to prevent damage to other treatment facilities. Since wastewater streams vary in pH from 1.5 to 12.0, the neutralization method is a function of the process of wastewater separation. Extreme fluctuations in the pH occur and, as a result, automated systems are used to adjust the pH and lessen operating costs.

Since wastewater temperatures are high compared to receiving surface waters, wastewater cooling is part of the pretreatment process. High temperatures result in reduced efficiency in the biological treatment process. Several cooling methods are used: towers, spray ponds, cascade channels, and detention ponds. Cooling towers and cascade channels may, however, aggravate the foaming problem accompanying pulp and paper mill wastewater treatment. The foam is controlled by cold water sprays and antifoam agents.

(2) Primary Treatment

Primary treatment is mainly responsible for the removal of suspended solids. Certain wastewater colloidal materials and dispersant-type chemicals inhibit gravity settling of suspended solids. Flocculation of the wastewater, with or without flocculating chemicals (alum, FeC13, polyelectrolytes), aids in the removal of suspended solids by gravity settling or dissolved air flotation. Settling lagoons or gravity clarifiers are used. Very fine fibers and solids from sulfite mills are removed by air flotation. The BOD removed is mainly the organic and fibrous materials that settle out.

Equalization facilities are commonly used between primary and secondary treatment to control variations in mill wastewater, flows and characteristics (pH or temperature).

(3) Secondary Treatment

Secondary treatment is mainly involved with the removal of soluble BOD, using biological treatment processes. Prior to treatment, nutrients vital to the existence of a balanced biological community are added — mainly N and P in the forms NH_3 and $H_3 PO_4$. Nutrient starvation could result in lower removal efficiencies and poor settling characteristics in the biological sludge.

The activated sludge process for BOD removal is implemented by contacting wastewater with a biological population in the presence of dissolved oxygen. Organic materials are thus removed from the water. Gravity settling removes the biological mass which returns to the beginning of the process to sustain it. In the contact-stabilization modification of this process, the biological organisms, after settling out and being transported to a separate aerated stabilization basin, are returned to the wastewater and then finally removed.

Eighty-five percent BOD removal is attainable with a process time of 4 to 6 hours for a mixed liquid having a suspended solids concentration of 2,000 to 3,500 mg/l. The contact-stabilization modification is particularly applicable to integrated Kraft mill effluents.

Trickling filters having biological growths remove waste organics as the wastewater flows through the media. However, this method has a lower BOD removal efficiency than the process previously discussed.

Another biological treatment method is the use of lagoons or stabilization ponds where low concentrations of biological solids are maintained to remove BOD. An aerated lagoon is capable of removing 40 to 70 percent of the BOD present.

Irrigation disposal is also used. Operational problems — runoff, stream pollution, freezing of wastewaters during winter — limit the applicability of this approach. However, 60 percent of the BOD can be removed before the wastewater reaches groundwater levels.

(4) Tertiary Treatment

Tertiary treatment is used to obtain removal of COD and suspended solids, as well as further removal of BOD, color, dissolved solids, and bacteria.

From a water pollution standpoint, lignins (as dissolved color) and bacteria (in concentrated communities) are of primary consideration. Tertiary treatment has not been very successful in removing these pollutants.

The most widely used facility for tertiary treatment is the holding pond. Additional BOD and COD removal by limited biological activity, as well as the removal of solids by extended detention and bacterial flocculation, occur. Aerobic conditions are required. Biological filtration and irrigation methods are also a part of tertiary treatment.

To date, neither chlorination nor ozonation has been practical for bacterial removal because of the high chemical demands and relatively high wastewater flows.

Color removal has been achieved by activated carbon absorption and foam separation with a 90 percent removal efficiency.

Inorganic solids removal is achieved by several tertiary treatment methods: electrodialysis, reverse osmosis, and ion exchange. Combinations of methods have been proposed.

(5) Other Methods

In addition to the four general treatments of wastewater, several other treatment operations may be conducted. Among these is sludge disposal, strong waste disposal, and by-product recovery.

- Sludge Disposal—the handling, dewatering, and disposal of primary and secondary sludges—either together or separately. Several dewatering methods are used: vacuum filtration using conditioning chemicals, centrifugation, sludge presses, drying beds, and sludge lagoons. The selection of method depends on sludge characteristics, land availability, ultimate disposal considerations, and proportion and secondary sludges. Landfilling or incineration of primary and secondary sludges is common.

- Strong Wastes Disposal—deep well disposal of liquor and pulp washer water. The effectiveness is dependent on geological formations at the mill location and the amount of waste discharged. Another method is dilution of spent liquors for land application — having similar factors as in irrigation disposal to define its effectiveness and their spray application to land. However, runoffs cause significant damage to receiving stream conditions because of high BOD and solid concentrations.

- Waste Treatment By-Products—Several organic by-products can be recovered from the cooking liquor

> resulting from various types of pulping operations. They include turpentine, oil, yeast, alcohols, and dimethyl sulfoxide (DMSO). Bark by-products include roofing felts, thermal insulation materials, and wrapping paper. The sulfite spent liquor can be used to produce insecticides, tanning agents, reinforcing agents, reinforcing agents in rubber, cement dispersing agents, etc.

By-products are not, at present, obtained from sludges resulting from mill wastewater. However, possible future by-product development includes: (1) fiber recovery from primary sludge, (2) drying activated sludge for use as a fuel supplement, and (3) processing activated sludge as an animal food supplement or commercial fertilizer.

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APPENDIX A-5
SIC 28→CHEMICALS AND ALLIED PRODUCTS

INDUSTRIAL ORGANIC CHEMICALS

1. GENERAL CHARACTERISTICS

The classification of industrial organic chemicals is generally defined in SIC codes 2815 and 2818. These classifications establish a middle ground between the processes which produce basic raw materials from petroleum refining and the industries which use organic chemicals to produce finished products. The distinction is certainly not clear cut. The basic processes for production of raw materials from coal are included in these two classifications, and some of the outputs are used commercially as finished products.

Any discussion of these two classifications as a separate entity is further complicated by the fact that the classifications do not define a given type of industry or plant operation. In the first place, it is common to find plants which combine products of organic chemicals in these classifications either with refining operations or production of final products in a number of other industrial classifications. Secondly, the range of organic chemicals included is so broad and the production processes so varied that there are entire industrial groups which specialize in producing only a few items. Considering that there are several thousand chemicals of commercial importance produced, the combination and permutations of combined product lines is quite large. For example, in 1969, some 1,500 different cyclic-intermediate organic chemicals were produced by about 215 different companies in an unspecified number of different plant locations. The number produced by a given company ranges from more than 10 percent of the total to a single compound.

(1) SIC 2815—Cyclic Intermediates, Dyes, Organic Pigments (Lakes and Toners), and Cyclic (Coal Tar) Crudes

This industry comprises establishments primarily engaged in manufacturing cyclic organic intermediates, dyes, color lakes and toners, and coal tar crudes. Important products of this industry include:

- Derivatives of benzene, toluene, naphthalene, anthracene, pyridine, carbazole, and other cyclic chemical products
- Synthetic organic dyes
- Synthetic organic pigments
- Cyclic (coal tar) crudes, such as light oils and light oil products; coal tar acids; and products of medium

and heavy oil such as creosote oil, naphtholene, anthracene, and their higher homologues and tar.

Establishments primarily engaged in manufacturing coal tar crudes in chemical recovery ovens are classified in SIC 3312, and petroleum refineries which produce such products in SIC 2911.

The industry is concentrated in the east coast area with 65 percent of the firms in this region. As of 1968, the middle atlantic division, in particular, contains 45 percent of all the establishments as documented below.

	Establishments (1968)	
Division	Total	20 or More Employees
New England	17	5
Middle Atlantic	78	46
East North Central	26	20
South Atlantic	20	14
East South Central	10	7
West South Central	14	11
Pacific	8	3
Total	173	106

The total number of establishments has grown considerably over the past decade. A 50 percent growth has increased the total number of firms from 115 in 1958 to 173 in 1968. In comparison,the total employment has grown relatively little from 28,300 in 1958 to about 30,000 by 1968.

There is a considerable variation in industry size as indicated below. However, 7 firms, comprising only 4 percent of the total number of firms,employ over 40 percent of the total industry employees.

Size of Establishment (No. of Employees)	No. of Establishments	Total No. of Employees
1 - 4	26	Less than 50
5 - 9	20	100
10 - 19	24	300
20 - 49	27	900
50 - 99	16	1,100
100 - 249	37	5,800
250 - 499	13	4,500
500 - 999	7	5,100
1,000 - 2,499	7	12,100
	177	29,950

The industry has experienced a 10-year growth (1958 to to 1968) in both total value of shipments and value added by manufacture. Value of shipments have grown over 70 percent from \$934.4 million to \$1,596.8 million, while value added has risen more than 80 percent from \$403.1 million to \$729.5 million.

Value of shipments of the cyclic intermediates and crudes industry in 1967 included shipments of cyclic intermediates and crudes (primary products) valued at \$1,092.1 million, shipments of other products (secondary products) valued at \$412.7 million, and miscellaneous receipts of \$91.9 million. Secondary products shipped by this industry in 1967 consisted mainly of industrial organic chemicals (\$168.4 million) and industrial inorganic chemicals (\$74.6 million).

Other industries shipping cyclic intermediates and crudes (primary products) consisted mainly of SIC 2818, Industrial Organic Chemicals (\$360.2 million), SIC 2911, Petroleum Refining (\$60.5 million), and SIC 2821, plastic materials and resins (\$42.8 million).

(2) SIC 2818—Industrial Organic Chemicals, Not Elsewhere Classified

This industry comprises establishments primarily engaged in manufacturing industrial organic chemicals, not elsewhere classified. Important products in this industry include:

- Noncyclic organic chemicals such as acetic, chloroacetic, adipic, formic, oxalic and tartaric acids and their metallic salts; chloral, formaldehyde, and methylamine
- Solvents such as amyl, butyl, and ethyl alcohols; methanol; amyl, butyl and ethyl acetates; ethel ether, ethylene glycol ether and diethylene glycol ether; acetone, carbon disulfide and chlorinated solvents such as carbon tetrachloride, perchloroethylene, and trichloroethylene
- Polyhydric alcohols such as ethylene glycol, sorbitol, pentaerythritol, synthetic glycerine
- Synthetic perfume and flavoring materials such as coumarin, methyl salicylate, saccharin, citral citronellal, synthetic geraniol, ionone, terpineol, and synthetic vanillin

- Rubber processing chemicals such as accelerators and antioxidants, both cyclic and acyclic
- Plasticizers, both cyclic and acyclic, such as esters of phosphoric acid, phthalic anhydride, adipic acid, lauric acid, oleic acid, sebacic acid, and stearic acid
- Synthetic tanning agents such as naphtalene sulfonic acid condensates
- Chemical warfare gases
- Esters, amines, etc. of polyhydric alcohols and fatty and other acids.

About 46 percent of the total number of establishments are located on the eastern seaboard and in particular the middle atlantic division with over 27 percent of the firms. However, a considerable number of firms are also located in the east north central, west south central, and pacific divisions as shown on following page.

Division	Establishments (1968) Total	20 or More Employees
New England	36	14
Middle Atlantic	132	75
East North Central	80	46
West North Central	18	7
South Atlantic	55	30
East South Central	25	18
West South Central	80	50
Mountain	7	3
Pacific	55	25
	488	258

The 10-year growth (1957 to 1968) in the number of establishments has been better than 45 percent, from a total of 334 in 1957 to 488 by 1968. During this same period, total employment has grown over 65 percent, from 508,000 million to 844,900 million.

Although the large majority of establishments have fewer than 100 employees, there are a few large firms with over 1,000 employees. Twenty firms, representing only about 4 percent of the total number of firms, employ over 50 percent of the total number of employees (about 49,000 persons), as shown on the following page.

Size of Establishment (No. of Employees)	No. of Establishments	Total No. of Employees
1 - 4	125	200
5 - 9	49	300
10 - 19	46	600
20 - 49	69	2,100
50 - 99	50	3,500
100 - 249	70	11,100
250 - 499	38	13,500
500 - 999	21	15,100
1,000 - 2,499	13	21,800
2,500 or more	7	27,000
	488	95,200

The industry has experienced a 10-year growth (1958 to 1968) of over 100 percent in both total value of shipments and value added by manufacture. Value of shipments have grown about 105 percent, from $3,098.0 million to $6,377.8 million, while value added has grown about 107 percent from $1,725.8 million to $3,575.3 million.

Value of shipments and other receipts of the Industrial Organic Chemicals Industry in 1967 included industrial organic chemicals (primary products) valued at $4,461.2 million, shipments of other products (secondary products) valued at $1,705.2 million, and miscellaneous receipts of $211.4 million.

2. PRODUCTION STATISTICS

The best available data on the production of synthetic organic chemicals is contained in the annual reports of the U.S. Tariff Commission (Reference 1), which list chemicals and the companies which produce them. Production statistics on materials in these SIC code industries are contained in Table A-5-1.

Table A-5-1
Production Statistics

General SIC Code	Material Classification	Production 1969 (millions of pounds)	Production Percent Change from 1968	Number of Producers
2815	Tar	7,608	+ 5.4	13
2815	Tar Crudes	9,845	+ 3.5	
2818	Intermediates	25,014	+ 9.4	215
2815	Dyes	226	+ 2.9	48
2815	Pigments	54	+10.9	35
2818	Flavor and Perfume Materials	117	- 4.8	52
2818	Rubber processing Chemicals	313	- 2.7	34
2818	Plasticizers	1,331	+ 2.9	59
—	Miscellaneous Chemicals	67,525	+14.5	340

(1) Tar and Tar Crudes

The quantity of tar and tar crudes produced from coal belongs to SIC code 2815 while that produced from petroleum is in classification 2900 and discussed elsewhere. Although the products are essentially the same, the quantity produced from coal is generally small (except for naphthalene) and the process is quite different from that used with petroleum. Comparisons are given in Table A-5-2.

Table A-5-2
Tar and Crude Production

Material	Producer	Units	Production 1969
Tar	Coke ovens	1000 gal	768,766
Benzene	Coke ovens	1000 gal	101,695
Benzene	Petroleum	1000 gal	1,083,653
Toluene	Coke ovens	1000 gal	19,603
	Petroleum	1000 gal	739,855
Xylene	Coke ovens	1000 gal	5,246
	Petroleum	1000 gal	376,596
Napthalene	Tar distillers and coke ovens	1000 lbs	525,711
	Petroleum	1000 lbs	375,945
Creosote Oil	All	1000 gal	126,895

(2) Cyclic Intermediates

As noted earlier, there are some 1,500 cyclic intermediates manufactured in commercial quantities. The precursors of these compounds are primary intermediates produced from natural gas, petroleum refining, and coal tar distillations, which are discussed separately. The chemical versatility of hydrocarbons in modern chemical technology has resulted in a great deal of conflicting market statistics because it is almost impossible to avoid counting basic structures more than once as they enter the market as different products. Thus ethylbenzene is a standard item of commerce (a cyclic intermediate and a final product), but so also are the benzene and ethylene from which it was made.

Of the 1500 cyclic intermediates, 84 percent of the total pounds produced can be accounted for by 16 companies as shown in Table A-5-3.

(3) Organic Dyes and Pigments

Domestic synthetic dyes are derived in whole or in part from cyclic intermediates. About two-thirds of the consumption is used to dye textiles, about one-sixth to color paper, and the

Table A-5-3
Large Volume Cyclic Intermediates

Material	Production 1969, (million lbs)	Number of Producers
Ethylbenzene*	4,907	16
Styrene	4,648	13
Cyclohexane	2,232	13
Phenol	1,691	13
Cumene	1,687	13
p-Xylene	1,628	12
Dimethyl terephthalate	1,537	4
Terephthalic acid	1,045	3
O - Xylene	850	16
Phthalic anhydride	760	12
Cyclohexanane	704	6
Chlorobenzene	602	11
Straight chain alkylbenzenes	529	7
Nitrobenzene	484	7
Isocyanates	421	11
Aniline	334	7

* Does not include ethylbenzene consumed in continuous process styrene production.

remaining one-sixth to produce pigments and dye leather and plastics. In 1961, the production was 240 million pounds. Note that this is two orders of magnitude smaller than production of cyclic intermediates. In fact, the total production in this category is less than just the aniline production.

There are several thousand different synthetic dyes known and more than a thousand are being produced by about 48 manufacturing companies. Three chemical classes of dyes account for two-thirds of the total production:

Azo dyes	31.5%
Anthraquinone dyes	21.6%
Stilbene dyes	17.1%.

Production of organic pigments amounted to 61 million pounds in 1969, by essentially the same manufacturers.

(4) Miscellaneous Organic Chemicals

This classification (as defined in Reference 1) covers many of the organic chemicals classified in SIC 2818. Total production in this classification in 1969 amounted to 76 million pounds, or three times the amount of cyclic intermediates. There are 340 companies involved in producing these materials.

The largest classes of cyclic materials were lubricating oil additives and synthetic tanning materials. In the acyclic groups, the largest classes were halogenated hydrocarbons, the nitrogenase compounds, monohydric alcohols, and aldehydes and ketones. Taken together, these classes represent 2/3 of the production.

In Table A-5-4,the major classification and the total production are shown, together with the members of each class with the largest production. Of the many hundreds of individual compounds produced, more than two-thirds of the production is accounted for in 25 compounds.

(5) Rubber Processing Chemicals

These are the organic compounds added to natural and synthetic rubbers to provide qualities necessary for conversion into finished rubber goods. Total production was about 300 million pounds in 1969, or less than the production of many individual chemicals in the other groups above. Thirty-four companies are involved in producing these compounds.

In the cyclic materials, which totaled 255 million pounds, 110 million pounds was in amino antioxidant compounds and 42 million pounds of phenolic and phosphite antioxidants.

Table A-5-4
Production of Miscellaneous Organic Compounds

	Billions of lbs		
Cyclic, total			1.90
Lube oil additives		.58	
Tanning materials		.40	
Other		.92	
Acyclic, total			73.81
Cellulose esters and ethers		1.15	
Cellulose acetate	.83		
Lubricating oil additives		.50	
Nitrogeneous compounds		13.29	
Acrylonnitrile	1.16		
Hexamethylenediamine	.66		
Acetone cyanohydrin	.54		
Urea	5.94		
Acids, acyl halides, and anhydrides		5.75	
Acetic acid	1.77		
Acetic anhydride	1.68		
Adipic acid	1.22		
Salts of organic acids		.25	
Aldehydes and ketones		9.99	
Acetaldehyde	1.65		
Acetone	1.52		
Formaldehyde	4.40		
Alcohols, monohydric		11.15	
Ethyl alcohol	2.36		
Isopropyl alcohol	2.01		
Methanol	4.21		
Polyhydric alcohols		5.53	
Ethylene glycol	2.57		
Propylene glycol	.46		
Esters of monohydric alcohols		2.28	
Halogenated hydrocarbons		16.19	
Carbon tetrachloride	.88		
Chloroethane	.68		
1.2 Dichloroethane	6.04		
Tetrachloroethylene	.64		
Trichloroethylene	.60		
Vinyl chloride	3.74		
All other		7.73	
Ethylene oxide	3.41		
Propylene oxide	1.78		
Phosgene	.51		
Rounded Totals	51.3	75.7	75.7

(6) Plasticizers

These are organic chemicals added to plastics and resins to modify their properties. Total production in 1969 was 1,382 million pounds. A total of 59 companies were involved in this production.

Cyclic plasticizers accounted for 1,023 million pounds of the total. Two compounds, di(2-ethylhexyl) phthalate and diiso-octal phthalate accounted for 438 million pounds or 42.8 percent of the cyclic production, or 31.7 percent of all production.

The acrylic plasticizers accounted for 359 million pounds of the total. Of this, complex linear polyesters amounted to 54 million pounds and epoxidized esters 104 million pounds.

The production by type material is shown in Table A-5-5.

3. PRODUCTION PROCESSES AND WASTE CHARACTERISTICS

All organic chemicals of industry can be synthesized from hydrocarbons. In the early years, hydrocarbon materials were obtained from coal. However, this source is inadequate to support the needs of a modern industrial economy and since WW II, the primary raw

Table A-5-5
Plasticizer Production

	Millions of lbs	
Cyclic, total		1,022
Phosphoric acid esters	67	
Phthalic anhydride esters	884	
Trimellitic acid esters	8	
Other	65	
Acryclic, total		359
Adipic acid esters	66	
Complex linear polyesters	54	
Epoxidized esters	104	
Oleic acid esters	13	
Phosphoric acid esters	19	
Sebacic acid esters	10	
Steric acid esters	10	
Other	70	

material source is petroleum refining. The oil refining industry has changed their operations from pure unit operations to one involving many unit processes for reforming of crudes. Currently, about 5 to 6 percent of the petroleum production is going into organic or petro-chemicals.

(1) Tar and Tar Crudes

This discussion is limited to coal derived products. Tar and tar crudes are produced by destructive distillation of coal, often in the production of coke for steel making. The products obtained are dependent on the type of coal used, the method employed, and the operating conditions. Consequently, the products are to some degree dependent on product demand. Currently, the two main objectives in the primary distillates of crude tar are to obtain a pitch or refined tar residue of the desired softening point and to concentrate, as far as possible in certain fractions, those components which are subsequently to be recovered. In the case of the vertical continuous retort, the main aim is to concentrate the phenols, cresols, and xylenols in the carbolic oil fraction, whereas, in the processing of coke-oven tar, the main objective is to concentrate naphthalene and anthracene in the napthalene oil and anthracene oil, respectively. The degree of fractionation employed is generally no better than that required to achieve these purposes. The number of fractions is usually below 7. Table A-5-6 indicates typical fractions that might be taken and the generally recognized product names. The boiling ranges and yields, however, will vary with each plant, its design, the nature of the crude, and the secondary refining operations. It should also be noted that there are no universally recognized names for the fractions and that the same term in different plants may refer to two different boiling ranges. The type products to be derived from each fraction are illustrated in Figure A-5-1.

In the fraction distilled up to 150°C, one method of further refining consists of washing with a 2 to 4 percent concentrated sulfuric acid. This produces a waste acid stream contaminated with organics which consist of sulfonated non-aromatics and thiophene derivitives. Alternatively the fraction is treated with a cobalt molybdate-on-alumia catalyst and solvent extraction to remove these same impurities. The benzol forerunnings contain carbon disulfide and cyclopentadiene. These forerunnings were formerly treated to recover the latter products, since cyclopentadiene was the starting material for Aldrin ® and Dieldrin ® insecticides.

Table A-5-6
Typical Fractions Taken in Continuous Tar Distillation to Medium-Soft Pitch

	Type of Tar					
	Continuous Vertical Retort			Coke Oven		
Fraction	Names	Boiling Range (^{o}C)	Wt (%) of Crude Tar	Names	Boiling Range (^{o}C)	Wt (%) of Crude Tar
1	Crude benzole, light oil	106-167	2.4	Crude benzole, light oil	99-160	0.6
2	Naphtha, Carbolic oil, Phenolic oil	167-194	3.1	Naphtha, light oil,	168-196	2.9
3	Heavy naphtha, Carbolic oil, Naphthalene oil	203-240	9.3	Naphthalene oil	198-230	14.6
4	Naphthalene oil	215-254	3.5	Wash oil, Benzole absorbing oil, light creosote	224-286	2.8
5	Wash oil, Benzole absorbing oil, light creosote	238-291	10.2	Anthracene oil, heavy creosote heavy oil	247-355	8.0
6	Creosote	271-362	11.5	Heavy oil	323-372 (90%)	9.5
7	Heavy creosote,	285-395 (50%)	12.1			
Residue	Medium-soft pitch		40.5	Medium-soft pitch		56.6
Liquor and losses			7.4			5.0

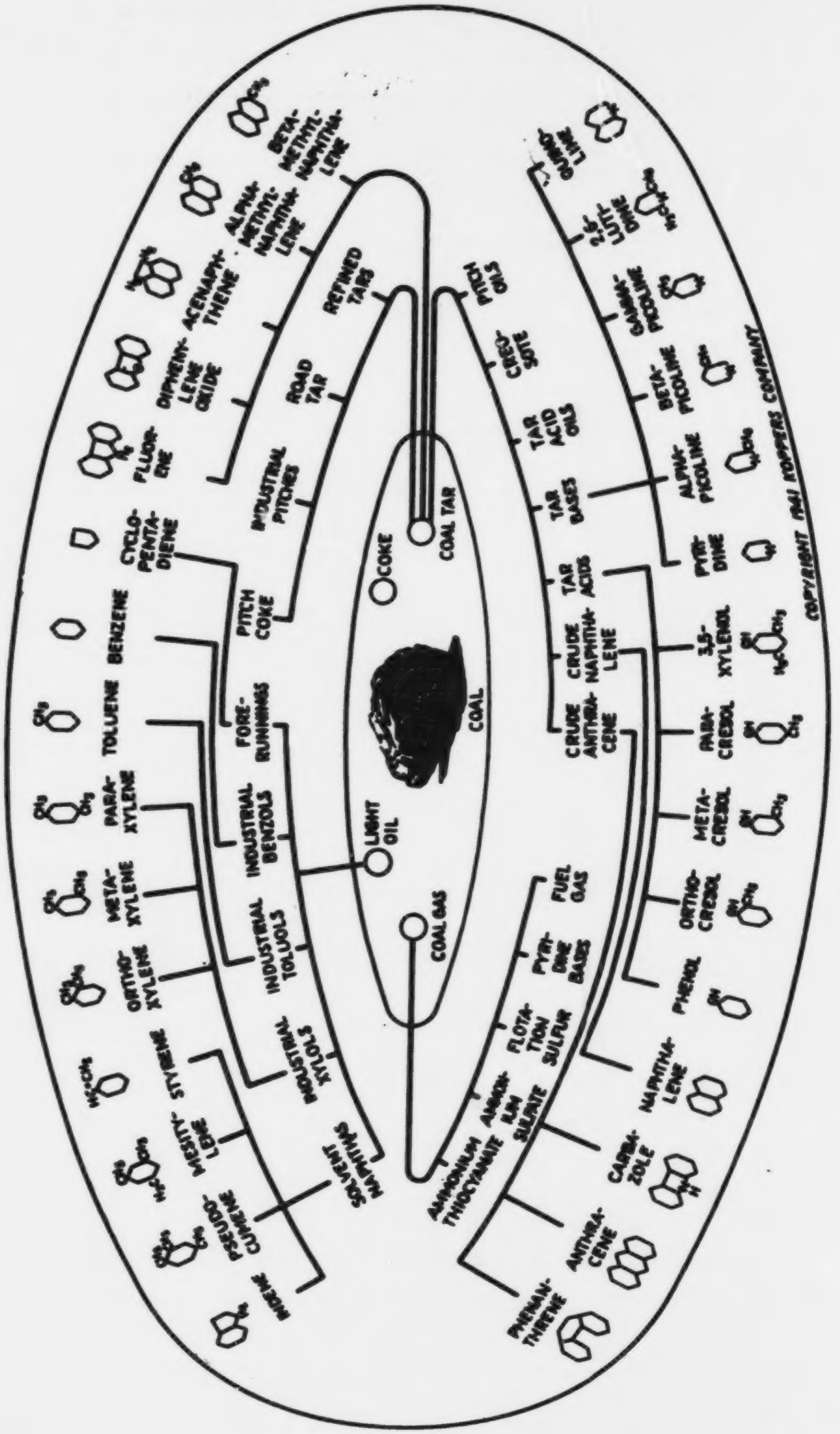
COAL
COKE
COAL TAR
LIGHT OIL
COAL GAS
PITCH COKE
INDUSTRIAL PITCHES
ROAD TAR
REFINED TARS
PITCH OILS
CREOSOTE
TAR ACID OILS
TAR BASES
TAR ACIDS
CRUDE NAPHTHALENE
CRUDE ANTHRACENE
FORE-RUNNINGS
INDUSTRIAL BENZOLS
INDUSTRIAL TOLUOLS
INDUSTRIAL XYLOLS
SOLVENT NAPHTHAS
FUEL GAS
PYRIDINE BASES
FLOTATION SULFUR
AMMONIUM SULFATE
AMMONIUM THIOCYANATE
INDENE
PSEUDO-CUMENE
MESITYLENE
STYRENE
ORTHO-XYLENE
META-XYLENE
PARA-XYLENE
TOLUENE
BENZENE
CYCLO-PENTADIENE
FLUORENE
DIPHENYLENE OXIDE
ACENAPHTHENE
ALPHA-METHYLNAPHTHALENE
BETA-METHYLNAPHTHALENE
QUINOLINE
2,6-LUTIDINE
GAMMA-PICOLINE
BETA-PICOLINE
ALPHA-PICOLINE
PYRIDINE
3,5-XYLENOL
PARA-CRESOL
META-CRESOL
ORTHO-CRESOL
PHENOL
NAPHTHALENE
CARBAZOLE
ANTHRACENE
PHENANTHRENE
COPYRIGHT 1941 KOPPERS COMPANY

FIGURE A-5-1
Products Derived from Coal

Source: Koppers Co., Inc.

These forerunnings are now disposed of as wastes (with the restrictions on organochlorine insecticides), principally by burning.

In the fraction distilled in the 150-200°C range, the pyridine bases, napthas and coumarone resins are produced. The pyridine bases can be extracted from this fraction with successive washes of 10 percent aqueous caustic soda (to remove phenols) followed by slight excess of 25-35 percent aqueous sulfuric acid in which the bases are soluble. The acid is neutralized with an alkali base to render the pyridine fraction insoluble, producing a saturated aqueous solution as waste. The naptha fraction is sometimes treated with sulfuric acid which produces a waste. The coumarone resin fraction is reacted with a boron trifluorine catalyst complexed with acetic acid or phenol to produce coumarone resin products.

The fraction distilling in the 200 to 250°C range currently produces the most valuable chemicals, the carbolic and naphthalene oils. The carbolic fraction (or tar acids or phenol fraction) are separated by extraction with an excess of 10 percent aqueous caustic. The carbolic fraction is steam distilled and then "sprung" in a "springing tower" by treating with a countercurrent flow of carbon dioxide. The springing tower product separates into two layers, a layer of crude tar acids and an aqueous waste solution of sodium carbonate containing tar acids. The crude tar acid layer is treated with either sulfuric acid or more carbon dioxide producing more aqueous waste of either sodium sulfate or bicarbonate. The sodium carbonate/bicarbonate solution is treated with quicklime (CaO) to recreate the caustic solution which in turn produces a calcium carbonate precipitate (lime mud) that is removed by filtration or precipitator. This lime mud is contaminated with tar acids, which are toxic.

The naphthalene in the 200 to 250°C fraction is the most abundant single compound in coke oven tar. It is refined in a number of ways but principally by crystalization and distillation. Distillation of product destined for production of phthalic anhydride must be desulfurized by treatment with sulfuric acid, metallic sodium or catalytic refining, which produce wastes. In any case, napthalene product is washed with dilute caustic, producing a toxic waste.

No tar chemicals are extracted commercially from the 250-300°C distilling fraction. Oil in this range is used in creosote blends.

Fractions distilling in the range 300-350°C contain the anthracene oils composed of 12-25 percent anthracence, 20-35 percent phenanthrene, and 7-15 percent carbazole. The waste associated with this fraction were not identified in this study.

(2) Cyclic Intermediates

1. Aniline

There are three production processes for aniline (Reference 2):

- Iron reduction of nitrobenzene
- Ammonolysis of chlorobenzene
- Vapor phase hydrogenation of nitrobenzene.

In the first, or iron reduction process (which is being superseded by vapor phase hydrogenation), 250 pounds of 30 percent hydrochloric acid solution and 3,200 pounds of iron borings are consumed per ton of aniline. These appear as waste liquor solutions of HCl and ferrous chloride ($FeCl_2$) and ferric oxide (Fe_3O_4) sludges. A second type aniline contaminated waste, tar waste, is produced as bottoms from the final product distillation purification step. Yields are 90 to 95 percent. Any waste contaminated with aniline is poisonous and toxic, and is a problem particularly because aniline is absorbed through the skin.

In the second process, ammonolysis of chlorobenzene, an aqueous solution of ammonia is reacted at high pressure. A by-product of a mole of ammonium chloride per mole of aniline is produced in aqueous solution, contaminated with aniline. The active catalyst is cuprous chloride made by reacting the by-product ammonium chloride with cuprous oxide. Consequently, the waste streams are solutions of ammonium chloride or cuprous chloride in one to one molar quantities to the aniline compound. Aniline yields are 85 to 90 percent.

The vapor phase hydrogenation of nitrobenzene or third process is conducted in a fluid bed reactor with a copper catalyst on SiO_2. The process produces a mole of water per mole of aniline as a by-product which is an aniline contaminated waste stream. Bottom purges from the crude aniline still used in product purification, consist of tars and other materials contaminated with aniline. Aniline yields are 98 percent.

2. Alkybenzene, Cumene and Ethylbenzene

These three materials are discussed together because all are produced by alkylation of benzene in chemically related reactions. All involve the reaction of an olefin with benzene in reactions catalyzed with a protenic acid (sulfuric acid, hydrogen fluoride, phosphoric acid) or by a Friedel-Crafts type of catalyst (aluminum cloride-hydrogen chloride, boron fluoride). A summary of the processes, catalysts and yields is given in Table A-5-7.

Multiple alkylations occur in these reactions. In the case of ethylbenzene, the polyalkylated material is recycled for transalkylation, but 2 percent of the feed is converted to higher polyalkylated products and olefin polymers which are removed as tars. All the alkylation reactions, therefore, lead to production of high molecular weight by-product tars resulting from condensation of the olefin feed and polyalkylation of the benzene. In addition

Table A-5-7
Summary of Alkylation Reactions

Material	Reactants	Catalyst	Catalyst Consumption	Yields
Ethylbenzene	Ethylene and benzene	$AlCl_3$-HCl	1-3 lbs/100 lbs product	92%
		H_3PO_4	1 lb/50 gal product	
		Alkar (BF_3)		High
Cumene	Prophylene and benzene	H_2SO_4	1 gal H_2SO_4/10-12 gal product	
		H_3PO_4	1 lb/200 lb product	90%
Dodecylbenzene	Propylene trimer and benzene	HF	- -	
		$AlCl_3$-HCl	1-3 lb $AlCl_3$/ 150 lb product	- -
		H_2SO_4	1 lb H_2SO_4/ 0.87 lb product	- -

impurities in the olefin feed stocks (such as propylene or acetylene with the ethylene) lead to by-products which are removed as wastes.

Other wastes produced in the processes result from the catalysts and the water and caustic washes used to neutralize the product. The aqueous streams are caustic containing sodium sulfate, sodium chloride and aluminum chloride contaminated with product and by-products.

3. Chlorobenzene

Production of monochlorobenzene consists of reacting purified benzene with dry chlorine in the presence of such chlorination catalysts as ferric, aluminum and antimony chlorides. The reaction is exothermic, and is always accompanied by the production of minor amounts of ortho and para isomers of dichloro benzenes. In practice, the chlorination of benzene is always conducted as a three-product process producing monochlorobenzene and the two dichlorobenzene isomers.

Production of higher chlorinated benzenes is accomplished in related processes with changes in reaction conditions.

The catalyst is not consumed in the process. The by-product hydrogen chloride is recovered in wash towers as commercially usable acid and solids.

In efficiently operated continuous processes, the yield of monochlorobenzene is 95 percent and the by-product dichlorobenzene is also retained as a usable product. Consequently, no significant toxic wastes were specifically identified in this study, although it can be hypothesized that reaction residues will contain some quantities of higher chlorinated benzene which will enter waste streams.

4. Cyclohexane

Cyclohexane is obtained as a natural product from petroleum distillation and from hydrogenation of benzene. Manufacture from benzene is a liquid phase reaction of benzene and hydrogen on an alumina supported platinum catalyst containing a small amount of lithium salt. A nickel catalyst can also be used on sulfur free benzene. No toxic wastes were identified in this study except spent catalyst and the reaction produces cyclohexane of 99.9 percent purity.

5. Cyclohexanone

Cyclohexanone can be produced by catalytic air oxidation of cyclohexane, catalytic dehydrogenation of cyclohexanol or by oxidation of cyclohexanol. The oxidation of cyclohexane with manganese and cobalt acetate is the most common practice, which produces cyclohexanol as a salable by-product, or the reaction mixture is treated with aqueous nitric acid to directly produce adipic acid.

The catalytic dehydrogenation of cyclohexanol can be accomplished with a substance capable of taking up hydrogen such as phenol. The reaction in the presence of catalysts produces only quantitative yields of product since the hydrogenation of the phenol from the hydrogen liberated from cyclohexanol also produces cyclohexanone.

The oxidation of cyclohexanol is accomplished by passing oxygen diluted with inert gas through the liquid phase at 10 atmospheres pressure and elevated temperatures. Adipic acid is produced as a salable by-product. Yields were not identified and other oxidation products would be expected. Degree of commercial use of this process is not known.

The first two processes for cyclohexanone are not expected to produce significant toxic wastes beyond the spent catalysts.

6. Isocyanates

There are a large number of different isocyanates produced as intermediates in polymeric applications. Most of the materials are consumed in polyurethane foams, elastomers and coatings. For economic reasons, the reaction of amines with phosgene is used almost exclusively for isocyanate production. Details of processing vary somewhat with the specific aromatic or aliphatic isocyanate, but all commercial manufacturing processes seem to take the following approach. The appropriate amine is mixed with phosgene in an aromatic solvent and the resulting slurry is digested for several hours at progressively increasing temperatures. The final solution is fractionally distilled to recover hydrogen chloride by-product, phosgene and solvent for recycling, isocyanate product, and a distillation residue which is incinerated. The residues are carbamyl chlorides and ureas which may be polymeric. The wastes would be hazardous if not incinerated.

It should be noted that the intermediates to this process are compounds which are toxic, and that production of amines produces toxic wastes.

7. Nitrobenzenes

The basic manufacturing process is the classic nitration reaction of benzene with mixed concentrated nitric and sulfuric acids. The nitric acid is consumed, the sulfuric acid becomes diluted and is reconcentrated for recycle. The yield is 95 to 98 percent based on nitrobenzene. Waste steams contain toxic and explosive materials including:

- The steam strippings of the separated acid which contain benzene and 0.5 percent of the nitrobenzene yield
- The water washes of the crude product which contain nitrobenzene
- Residues from product distillation which contain dinitrobenzene and nitrophenol.

Newer production processes are based on techniques to directly react nitric acid and benzene without the sulfuric acid to act as a water scavenger. The newer processes have been operated at 99.3 percent conversion rates. The wastes in these processes would be as stated above for residues from product purification distillation.

8. Phenol

Natural phenol is extracted from coal tar but more than 96 percent of the phenol produced is synthetic. There are four primary production processes using benzene and one process using toluene.

About 50 percent of the U.S. production is based on the cumene process where the cumene is produced from benzene. Cumene is reacted with air in aqueous solution to form the hydroperoxide. Cumene is carried out of the reactor by the nitrogen gas waste stream. Cumene hydroperoxide is cleaved by mixing with dilute sulfuric acid to produce two products, phenol and acetone. The cleavage reaction mixture is distilled to separate unreacted cumene, acetone, and phenol, as well as the by-products a-methylstyrene, acetophenone (which are sold) and tars. The yield of phenol is 93 percent based on cumene and 84 percent based on benzene.

The Rashig-Hooker process accounts for about 17 percent of phenol production and is based on oxychlorination of benzene to produce monochlorobenzene, followed by hydrolysis of the chlorobenzene to phenol. This involved, self-contained, intricately cyclic process produces phenol in yields of about 84 percent based on benzene. The only by-product of this process are high-boiling materials designated as tars. This process is alleged to be in use at the Hasker plant at South Shore, Kentucky.

The sulfonation process was the first commercial synthesis process, and is still in use when the production plant can be located close enough to a paper plant to consume the by-product sodium sulfite. This process produces about 16 percent of U.S. production. In this process, benzene is reacted with sulfuric acid to form benzene sulfonate. The sulfonate is reacted with sodium hydroxide to form the sodium salt of phenol and sodium sulfite by-product in water solution. The sodium salt of phenol is reacted with carbon or sulfur dioxide to form phenol and a solution of sodium bicarbonate or bisulfate.

The product phenol is purified by distillation and the waste residue contains o-phenylphenol and p-phenylphenol.

The chlorobenzene hydrolysis process, operated by Dow Chemical, reacts monochlorobenzene with aqueous sodium hydroxide at high temperature and pressure in a tubular reactor to produce phenol. This process accounts for about 16 percent of U.S. production. The yield of useful products is about 93 percent based on chlorobenzene. Significant quantities of diphenyloxide, o-phenylphenol, and p-phenylphenol are produced as by-products and the process must be of a scale to enable recovery of these materials for sale to keep it economically competitive. The process produces phenol and phenoxide contaminated sodium chloride brines as wastes.

The Toluene Air Oxidation process is used by Dow Chemical at Kalama, Washington. In 1964 this plant was rated at 36 million pounds per year. Toluene is oxidized to benzoic acid with air using a soluble cobalt catalyst, in water. This reaction proceeds with 90 percent yield and produces a formic acid waste stream in water solution.

The benzoic acid is purified by distillation and the residue still bottoms create a waste stream of tars. The benzoic acid is oxidized with steam and air in the presence of 1 to 2 weight percent copper benzoate and 1 to 2 weight percent magnesium benzoate. The product phenol, carried out of the reactor with the steam and air, is purified by distillation. The reaction of benzoic acid with air is conducted at yields of 83 percent on benzoic acid and produces a tar waste stream, separated directly out of the reactor.

9. Phthalic Anhydride

This material is produced by the air oxidation of naphthalene or o-xylene. There are four basic reaction systems; a low and high temperature fixed bed reactor, fluidized bed and liquid phase reaction. The first three use vanadium pentoxide catalyst systems, and the fourth a bromine activated heavy metal catalyst. The low temperature fixed bed process produces relatively small amounts of by-products with an almost unlimited catalyst life. Yields are 82 percent of theory with naphthalene, and 73 percent with o-xylene.

The high temperature fixed bed is a U.S. development and used by Monsanto and Chevron Oil among others. By-products are higher, particularly maleic anhydride, then in the low temperature process. Yield with o-xylene is 72 percent of theory, and with naphthalene 65 percent.

Fluid bed oxidation accounted for 50 percent of U.S. production in 1967. In 1967, by-products using o-xylene were excessive but the problem was being given extensive study. By-products with naphthalene are small. Catalyst loss occurs and catalyst life is limited. The process is used by Badger, American Cyanamid and United Coke and Chemical.

The liquid phase oxidation in acetic acid solvent uses a mixed xylene feed to simultaneously produce phthalic, isophthalic and terephthalic acids. Yields of 88 percent with o-xylene are expected.

Each reaction system loses yield by process combustion of feedstocks. Each purifies the anhydride and the purification step produces a brittle, solid waste tar residue.

10. Terephthalic Acid and Dimethyl Terephthalate

These compounds are chemically similar to phthalic anhydride and the production processes correspond. The primary processes for terephthalic acid are as follows.

Nitric acid oxidation of p-xylene is reported to be used by DuPont. A liquid phase of p-xylene, 30 to 40 weight percent strength nitric acid and air are reacted to form terephthalic acid directly. The process converts up to 2 pounds of nitric acid per pound of p-xylene to oxides of nitrogen, so a nitric acid plant is required to convert the oxides back.

In the catalytic liquid phase air oxidation process, acetic acid is used as a reaction medium with bromine promoted heavy metal oxidation catalysts such as cobalt or manganese. This process is used by Amoco Chemicals Corporation. Eastman Chemical Products utilizes acetaldehyde as the catalyst activator. Mobil Chemical Company uses methyl ethyl ketone as the catalyst activator. This process produces a more pure product than the nitric acid system. The purity is better than 99% by weight and contains traces of the reaction intermediates, tolualdehyde, p-toluic acid, and 4-carboxybenzaldehyde.

Production of dimethyl terephthalate was undertaken because of the difficulty of converting terephthalic acid to polymer grade material. Terephthalic acid is reacted with methanol with a sulfuric acid catalyst to form this material. The product formed is purified by distillation or crystallization. It can also be produced by air oxidation in the liquid phase of p-xylene with a cobalt catalyst, to produce toluic acid; reaction of this material with methanol; the methyl toluate product again air oxidized with a cobalt catalyst; and the acid product again esterified with methanol. This process is used by Hercules.

By-products of dimethyl terephthalate production are toluate esters. This study did not find mention of other waste products but it can be hypothesized that quantities of tars are produced from the purification of both of these compounds.

11. Styrene

There are a variety of possible methods for reduction of styrene but all current production is believed to be based on dehydrogenation processes. The essence of the process consists of passing ethylbenzene mixed with superheated steam over a fixed iron oxide-potassium oxide pebble catalyst bed at high temperature to force elimination of a hydrogen molecule from the ethyl alkyl group. Part of the ethylbenzene feed is destroyed by thermal cracking and the reactor vent stream contains styrene product, benzene, ethylene, methane, hydrogen carbon dioxide, water, and other materials. Yields are about 90 percent, based on moles of product per moles of ethylbenzene. The styrene is purified by distillation with removal of benzene, toluene, water and unreacted ethylbenzene overhead, and tars and polymeric material removed as still bottoms. The condensed steam produces a water waste contaminated with benzene, toluene, styrene, ethylbenzene, formaldehyde, benzaldehyde, peroxides and other materials.

12. Xylenes

The xylenes are obtained from petroleum refining and are produced from reforming of selected naptha streams. The wastes associated with petroleum refining operations are discussed under that heading.

(3) Dyes

To attempt to define the production processes and wastes generated in the dye industry within a few pages is a hopelessly impossible task. Moreover, an accurate assessment and characterization of the toxic waste processed in this industry is needed because of the nature and quantity of wastes produced. This study was not able to satisfactorially address the problem. A gross summarization of basic characteristics follows.

There are two parts to dye manufacture:

- Preparation of intermediates
- Preparation of dyes.

The distinction is somewhat arbitrary, particularly since many of the cyclic intermediates presented in the previous section are dye intermediates.

1. Preparation of Intermediates

Figures A-5-2 to A-5-6 illustrate typical processing routes based on four key primary raw materials. The overall processing can be characterized as occurring in four steps. Step one involves attack on the aromatic

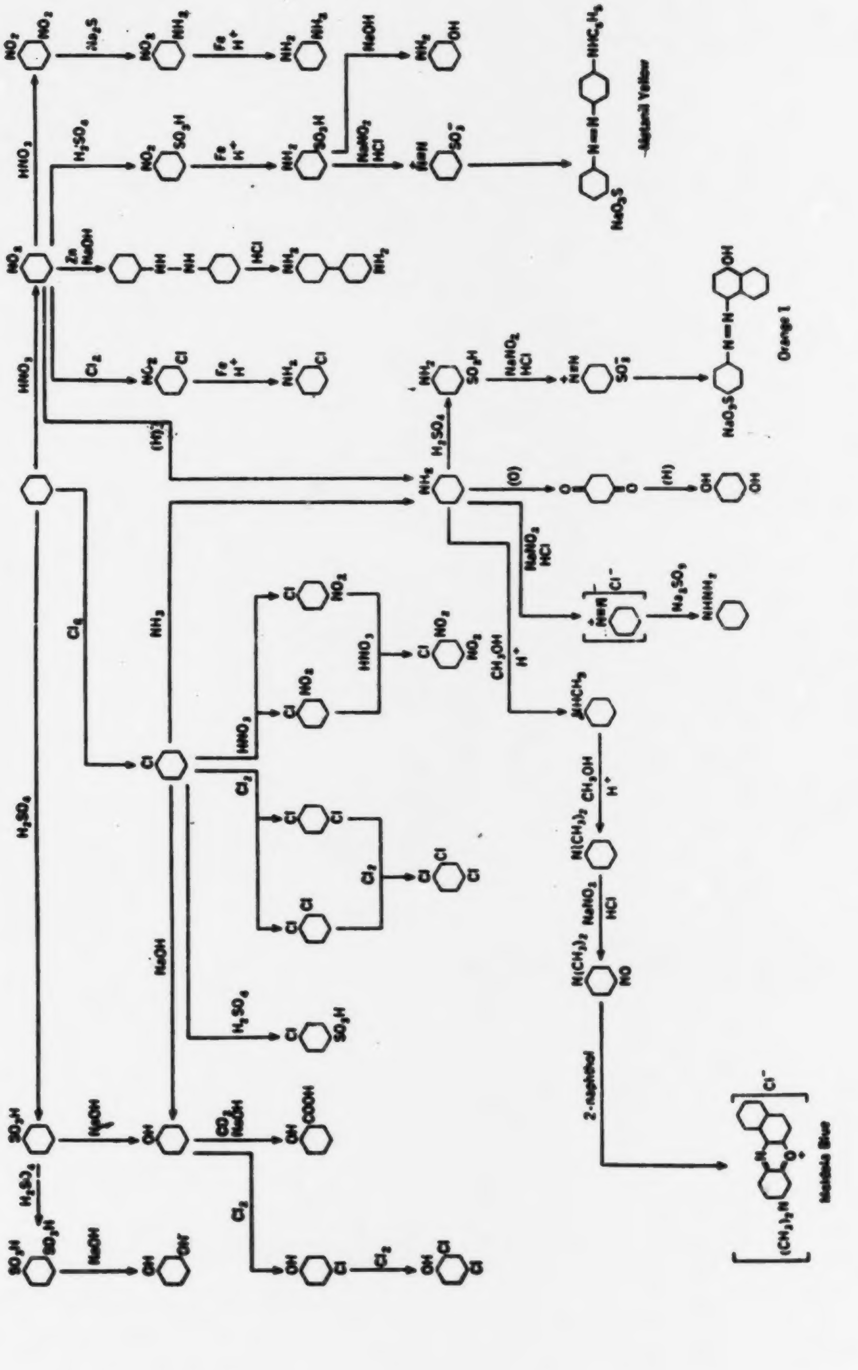
HNO₃
H₂SO₄
Cl₂
NH₃
NaOH
Na₂S
Fe H⁺
Zn NaOH
HCl
NaNO₂ HCl
(H)
(O)
CH₃OH H⁺
Na₂SO₃
CO₂ NaOH
2-naphthol
Metanil Yellow
Orange I
Meldola Blue

FIGURE A-5-2
Benzene Derivatives

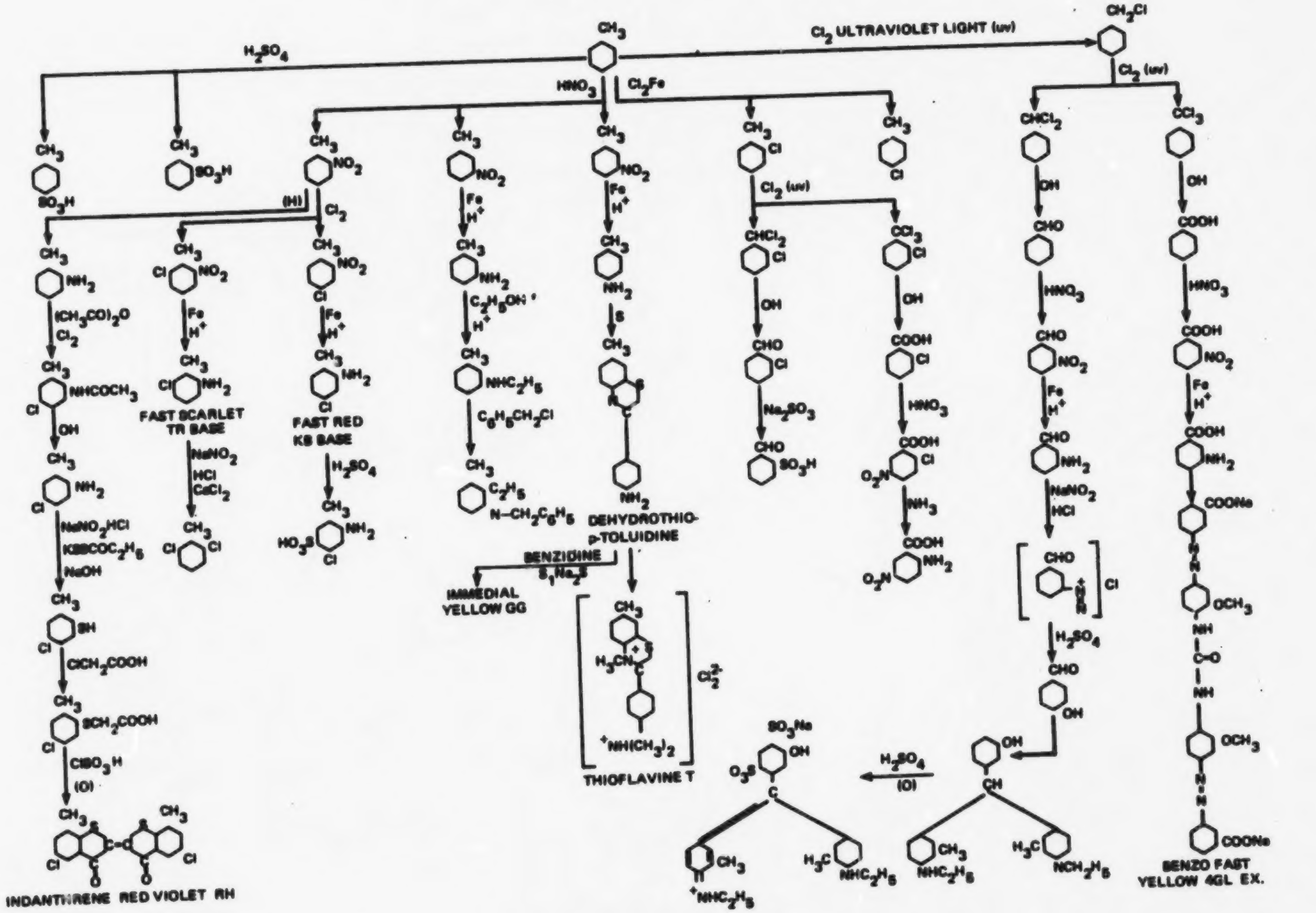
Cl2 ULTRAVIOLET LIGHT (uv)
H2SO4
HNO3
Cl2Fe
Cl2 (uv)
FAST SCARLET TR BASE
FAST RED KB BASE
DEHYDROTHIO-p-TOLUIDINE
BENZIDINE
IMMEDIAL YELLOW GG
THIOFLAVINE T
INDANTHRENE RED VIOLET RH
BENZO FAST YELLOW 4GL EX.

FIGURE A-5-3
Toluene Derivatives

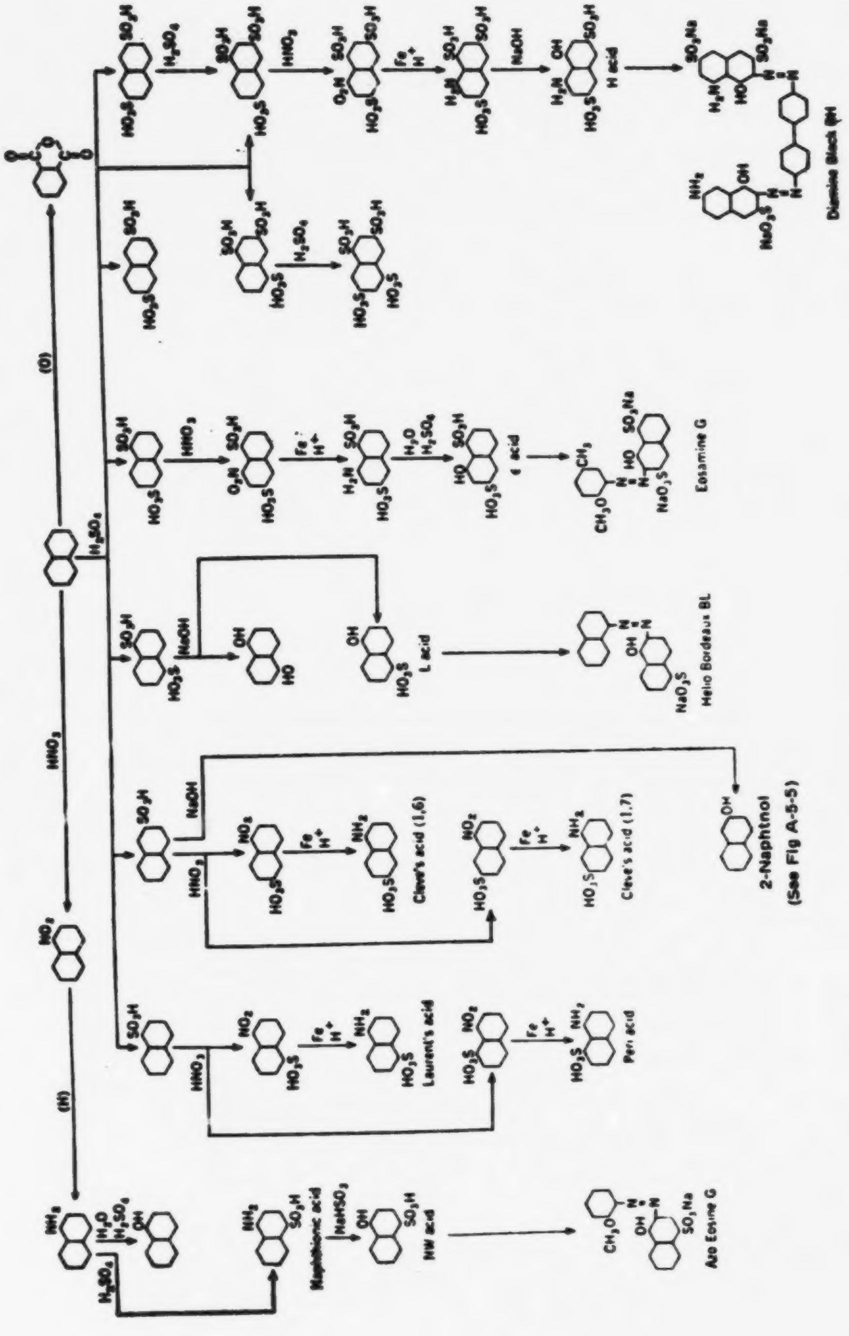
(O)
HNO₃
H₂SO₄
(H)
H acid
Diamine Black BH
ε acid
Eosamine G
L acid
Helio Bordeaux BL
Cleve's acid (1,6)
Cleve's acid (1,7)
2-Naphtnol
(See Fig A-5-5)
Laurent's acid
Peri acid
Naphthionic acid
NW acid
Azo Eosine G

FIGURE A-5-4
Naphthalene Derivatives

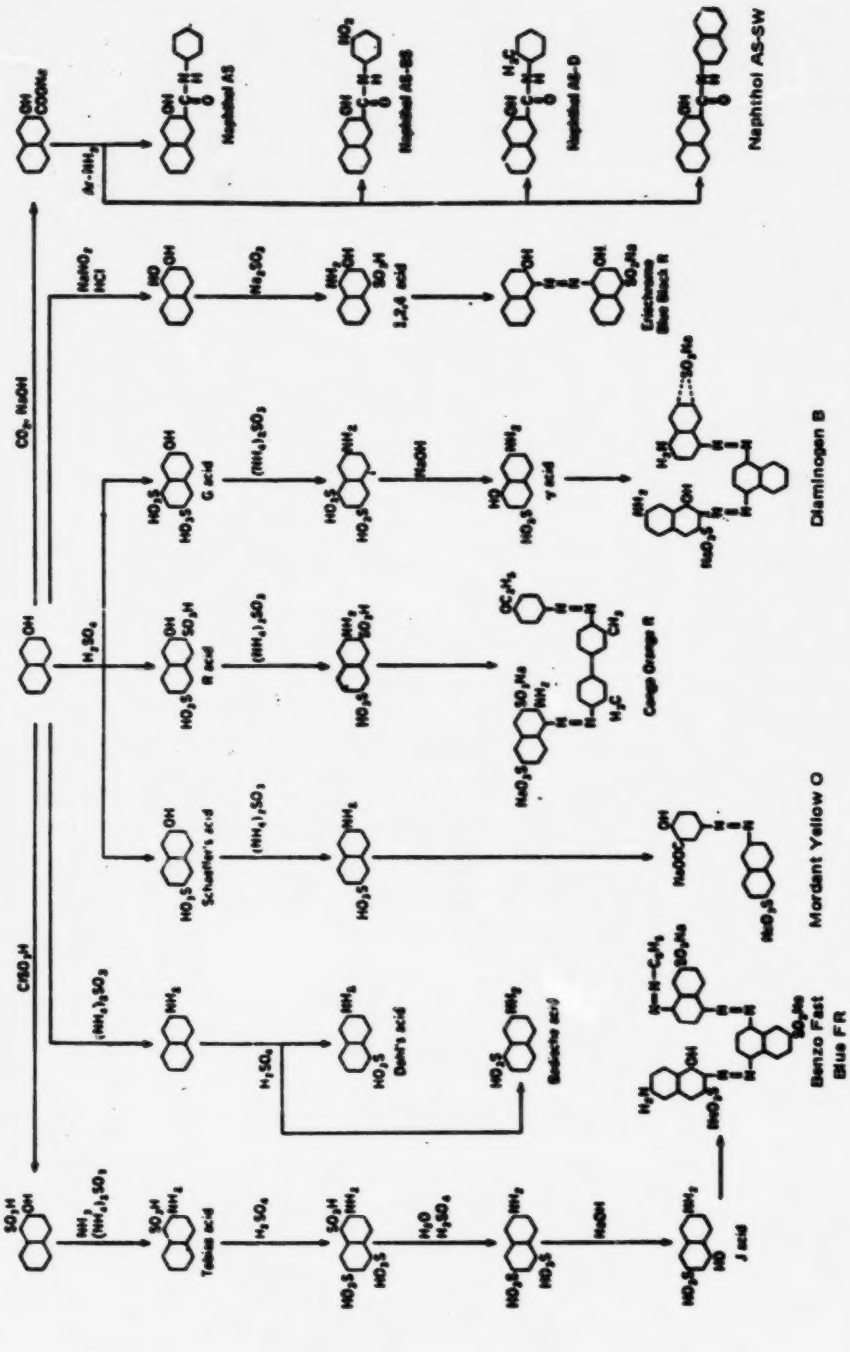
Naphthol AS
Naphthol AS-BS
Naphthol AS-D
Naphthol AS-SW
Ar-NH2
CO2, NaOH
NaNO2 HCl
Na2SO3
1,2,4 acid
Eriochrome Blue Black R
G acid
(NH4)2SO3
NaOH
Y acid
Diaminogen B
H2SO4
R acid
(NH4)2SO3
Congo Orange R
Schaeffer's acid
(NH4)2SO3
Mordant Yellow O
ClSO3H
(NH4)2SO3
H2SO4
Dahl's acid
Badische acid
Benzo Fast Blue FR
NH3 (NH4)2SO3
Tobias acid
H2SO4
H2O H2SO4
NaOH
J acid

FIGURE A-5-5
Naphthol Derivatives

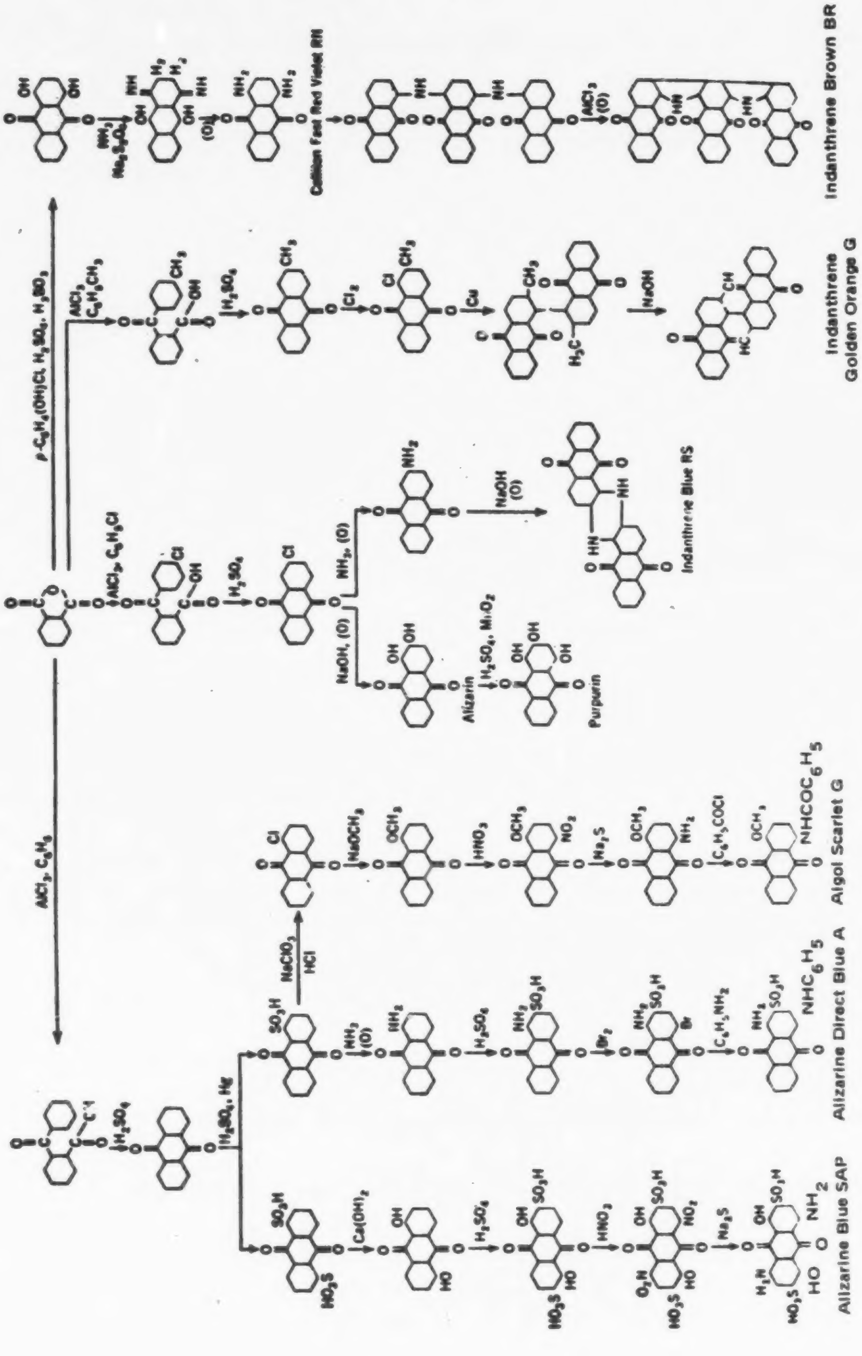
AlCl3, C6H6
p-C6H4(OH)Cl, H2SO4, H3BO3
AlCl3, C6H5Cl
AlCl3, C6H5CH3
H2SO4
H2SO4, Hg
Ca(OH)2
HNO3
Na2S
NH3 (O)
Br2
C6H5NH2
NaClO3 HCl
NaOCH3
C6H5COCl
NaOH, (O)
NH3, (O)
H2SO4, MnO2
NaOH (O)
Cl2
Cu
NaOH
AlCl3 (O)
Alizarine Blue SAP
Alizarine Direct Blue A
Algol Scarlet G
Alizarin
Purpurin
Indanthrene Blue RS
Indanthrene Golden Orange G
Cellitan Fast Red Violet RN
Indanthrene Brown BR

FIGURE A-5-6
Anthraquinone Derivatives

hydrocarbon raw material, introducing one or more groups. The most frequently used reactions are:

- Sulfonation
- Nitration
- Halogenation
- Friedel-Crafts
- Oxidation.

These type reactions and the waste stream they produce were described in the discussion of cyclic intermediates. Basically, most of those processes were step one activities, with respect to the dye industry.

Step two reactions involve replacement or conversion of substituents introduced by step one reactions by groups of higher reactivity which cannot be introduced directly. These step two reactions furnish the OH, NH_2, CH, OR, SR and NRR' groups. Such reactions produce salt and brine liquid wastes of Fe_2O_3 sludges, ammonium chloride solutions, zinc hydroxide precipitates, sodium sulfate solutions, as well as tars from purification steps.

Step three involves further modification or development of functional groups already introduced. The reactions used are dependent on the dye to be produced and involve the organic chemists' complete gambit of techniques.

Step four reactions are basically reactions which combine two intermediates to form products having a skeletal if not a complete dye structure. Typical reactions include diazotization and coupling, condensation and dimerization.

2. Preparation of Dyes

The preparation of dyes can be characterized by type used, by type material to be dyed, or by chemical similarity. When classed by chemical similarity, three types comprise two-thirds of all manufacturing:

- Azo
- Anthraquinone
- Stilbene.

Azo dye production involves diazotization of primary aromatic amines, followed by coupling with hydroxy or amino aromatic hydrocarbons and other aliphatic compounds.

The generalized procedure for diazotization and coupling is as follows. Sodium nitrite is added slowly to an acid solution of the amine. The nitrous acid produced reacts with the amine to complete the diazotization. The total mix is run into an acid or alkaline solution of the intermediate to be coupled (depending on the nature of the dye). After a time period varying from a few minutes to three days, sodium chloride is added to precipitate the dye, and the reaction mass is filtered. The solid dye remains in the filter and the liquid becomes a waste stream. This stream contains a salt solution of the acid used and can contain quantities of the organic reactants.

Quantities of wastes produced in azo dye manufacture can be illustrated by the material balance for producing 1,800 pounds of Chrome Blue Black U:

. Beta-napthol	730 pounds
. Sodium hydroxide (40%)	600 pounds
. Water	10,000 pounds
. Hydrochloric acid (20%)	500 pounds
. 1-amino-2-napthol-4-sulfuric acid	1,200 pounds

.	Sodium chloride	200 pounds
.	Copper sulfate hydrate	15 pounds
.	Sodium nitrite	365 pounds

Note that the sum of the two primary reactants, 6-napthal and 1, 2, 4 acid, total 1,930 pounds, which means that at least 130 pounds of these two reactants disappeared. Also note that everything except the product is sewered.

Anthraquinone dyes are based on synthesis of anthroquinone from phthalic anhydride. A variety of approaches are possible. If benzene is used with the anhydride, anthroquinone is produced directly. If chlorobenzene is used, chlorinated anthroquinone is produced, etc. Such reactions can produce aluminum chloride solution wastes, sulfuric acid wastes, etc. Subsequent processing of the anthroquinone can proceed in an infinite variety of ways with creation of large waste streams. For example, to produce 100 pounds of indanthrene yellow G requires processing:

.	Phthalic anhydride	148 pounds
.	Chlorobenzene (80%)	600 pounds

Aluminum chloride	300 pounds
H_2SO_4 (100%)	1,500 pounds
Ammonia (28%)	1,500 pounds
Nitrobenzene	2,000 pounds
Antimony pentachloride	700 pounds

The ammonia is 90 percent recovered and the nitrobenzene can be recovered as aniline, but note the quantities of other potential wastes.

(4) Tanning Materials

The most used synthetic tanning material is 2-napthalene-sulfuric acid condensed with formaldehyde. The acid is prepared by reaction of concentrated sulfuric acid on naphthalene. The reactor produces the 1-sulfuric acid which is hydrolyzed back to naphthalene and removed from the product by stream distillation.

(5) Halogenated Hydrocarbons

1, 2-Dichloroethane, important as a starting material for vinyl chloride, is produced by reacting chlorine with ethylene. To obtain high yields of the desired product without various side reactions, controlled reaction conditions and catalysts such as ferric, aluminum, copper, or antimony chloride are used. The reaction is conducted in either the gaseous or liquid phase. A process reacting a gaseous mixture of anhydrous hydrogen chloride, ethylene, and air in a fluidized bed of copper chloride impregnated catalyst, is used in coordination with a continuous vinyl chloride process and the first process above, to utilize the hydrogen chloride by-product of vinyl chloride production. 1, 2-dichloroethane is also obtained as a by-product in the production of ethyl chloride when chlorinating petroleum derived C_2 gases. Waste streams include dilute caustic with sodium chloride used to wash the product, and heavy ends from the purification distillation containing poly-chlorinated material.

Vinyl chloride is manufactured by two processes:

- Catalyzed hydrochlorination of acetylene
- Pyrolytic or alkaline dehydrohalogenation of 1, 2-dichloroethane.

In the acetylene process, dryed acetylene and anhydrous hydrogen chloride are mixed in an activated carbon filled chamber, and then passed through heated tubes containing mercuric chloride deposited on carbon to effect the reaction. A variety of other catalysts are used in mixture with mercury chlorides such as thorium, cerium, cadmium and potassium chlorides. Wastes produced include (1) the carbon in the mixing chamber saturated with chlorine and other impurities, (2) the spent catalyst suspended in carbon, and (3) ethylidene chloride and acetaldehyde by-products, as well as hydrated solid potassium hydroxide used to dry the product before distillation. Yields on acetylene are 99 percent.

Vinyl chloride is produced by dehydrohalogenation of 1, 2-dichloroethane. The 1, 2 dichloro is passed through tubes packed with pumice, or charcoal, or china clay, or titanium oxide, etc., at high temperature to effect removal of a hydrogen and a chlorine atom and produce the product. Wastes produced are hydrogen chloride which is recovered, and chlorinated tars. Yields are 95 to 96 percent on the 1, 2 dichloroethane.

Carbontetrachloride has many uses but is an important intermediate for dichlorofluoromethane. Many production processes are possible. Chlorinalysis, the chlorination of hydrocarbons at pyrolytic temperatures with simultaneous breakdown and chlorination of the molecular fragments, is used to produce this product. Large amounts of higher molecular weight by-products are formed and yields of carbontetrachloride are about 70 percent. The high temperature chlorinalysis can be operated to produce perchloroethylene in equal amounts, especially if the methane and chlorine reactants are run through a fullers earth catalyst bed. Wastes always include hydrogen chloride, higher molecular weight chlorinated co-products and chlorinated tars.

Carbontetrathloride can be produced by chlorination of carbon disulfide dissolved in carbontetrachloride and sulfur monochloride using an iron filings catalyst. Sulfur is produced and recovered to make additional carbon disulfide. This process produces no co-products or by-products.

Ethylchloride production principally occurs by two processes:

- Chlorination of ethane
- Hydrochlorination of ethylene

The chlorination of ethane occurs at high temperature and can be conducted in an inert fluidized bed at about 78 percent yield. By-products are ethylene which is recycled to produce ethyl chloride, and HCl. Hydrochlorination of ethylene can be done with HCl either at high temperature over thorium oxychloride catalyst suspended on silica with production of polymeric materials which eventually destroy the catalyst (waste product) or at normal temperatures in liquid phase with an aluminum chloride catalyst in 2 percent solution in ethylchloride.

Trichloroethylene can be produced by three prime processes:

- Aqueous alkaline processes
- Pyrolytic Processes
- Conversion of 1, 2-dichloroethane.

The starting material is tetrachloroethane (produced from acetylene or ethylene) and the first two processes are dehydrochlorination reactions. In the aqueous process, the raw material is reacted with hot calcium hydroxide, or sodium hydroxide, or ammonium hydroxide to remove an HCl molecule. Wastes include the respective chlorine salts of the hydroxides. Thermal dehydrochlorination is effected by passing the tetrachloro over barium chloride catalyst on activated carbon. Spent catalyst contaminated with chlorinated tarry material is produced as waste, along with heavy ends and tars from the product purification. The conversion of 1, 2dichloroethane is conducted as an oxychlorination at high temperature with air and chlorine over copper chloride catalyst on carbon. The reaction produces spent catalyst contaminated with tarry waste, and chlorinated tars from product purification.

Tetrachloroethylene for many years was produced by chlorination of trichloroethylene to pentachloroethane and dehydrochlorination with cadium hydroxide slurry (or other strong alkali) as described above, producing similar waste streams. The pentachloroethane can also be dehydrochlorinated thermally over thorium or copper chloride catalyst as described above, with similar wastes, and recovery of the HCl.

(6) Phosphorus Compounds

Phosphorus compounds are widely used as oil additives, insecticides, plasticizers, gasoline additives, flotation agents, stabilizers, antioxidants and surfactants. All of these different end users are based on compounds produced by similar types of production processes.

Three inorganic phosphorus compounds are principally used as reactants in commercial productions:

- Phosphorus trichloride
- Phosphorus oxychloride
- Phosphorus pentasulfide.

Each of these compounds will react with an organic aromatic or aliphatic alcohol to form mono-, di-, or tri-esters. If phosphorus trichloride is used, the products are phosphines; the oxychloride produces phosphates, and pentasulfide thiophosphates. When using the chlorides, production of the mono-, di-, or tri-ester is dependent on the reaction conditions and the use of a sequesting agent such as an amine, to tie up hydrogen chloride produced. By-products in reaction with phosphorus chloride's include the alkyl or aryl chloride, and either HCl or the alkali salt (such as ammonium chloride). Wastes include slimy solids which are polymerization products of the reaction.

Similar reactions between the pentasulfide and alcohols produce diesters, with hydrogen sulfide as a by-product.

Mono- and di-esters produced in the above reactions can be further processed to add an additional ester group of another type. This normally involves chlorination (to produce an intermediate) with production of hydrogen chloride as a by-product. Adding the additional ester can be accomplished either with production of hydrogen chloride or sodium chloride as by-product, depending on the mechanism selected.

The product materials are normally purified and separated from reaction mixtures by distillation. Since the compounds are subject to thermal degradation, distillation residues include slimy or glassy polymerization products as wastes.

(7) Fermentation Reactions

Because of similarities in waste disposal processes, the industrial organic chemicals manufactured by fermentation will be discussed together. There are five important compounds produced in this manner:

- Ethyl alcohol
- Glycerol
- Acetic acid
- Acetone - butyl alcohol
- Amyl alcohol.

Alcohol production by fermentation and from ethylene compete. Acetone, butyl alcohol, and acetic fermentation production have largely been superseded by synthetic processes.

1. Ethyl Alcohol

This compound is produced by yeast fermentation from a variety of starch and sugar containing natural products, in either batch or continous processes. The process consists of fermenting a mash and separation of the alcohol and related constitutents by distillation. This first distillation produces a waste known as slop or stillage, and it contains proteins, residual sugars, and some vitamin products; it is evaporated and sold as animal feed. The distilled product fraction contains alcohols and aldehydes which are separated in further distillations, producing product ethyl alcohol, and impure amyl alcohol and aldehydes as salable by-products.

2. Acetone and Butyl Alcohol

Production of these materials by fermentation has virtually ceased with development of synthetic routes and increased prices of grain and molasses feed stocks. The bacterium Clostridium acetobutylicum, in its action on starches produces a series of product compounds in the route to acetone, butyl alcohol and ethyl alcohol. Among these are acetyladehyde, acetic acid, acetyl-methyl-carbinol, and butyric acid, which are obtained as by-products or wastes. The three primary products, acetone, butyl and ethyl alcohol are produced in the ratios of 3:6:1. The process is as described above for ethyl alcohol, with the stillage from the fermentation dried and sold as feed. Other by-products are corn oil, germ meal and corn husks, all of which are sold, as well as carbon dioxide and hydrogen gases.

3. Acetic Acid

This acid can be manufactured by high temperature oxidation of ethyl alcohol which now is the dominant procedure. In fermentation production, a dilute solution of alcohol is converted to dilute (8 percent) acetic acid solution in 80 to 90 percent yields by Bacterium aceti. The process is economical only if there is a market for this dilute acid.

(8) Amination By Ammonalysis Reactions

This procedure is used for production of ethanolamines. Ethylene oxide is bubbled through aqueous ammonia solutions to produce the mixed mono-, di-, and tri-ethanol amines in 95 percent yield.

(9) Aliphatic Acetate Production

The acetates are produced by esterification reactions between the appropriate aliphatic alcohol and acetic acid, or by esterification of acetylene.

The reaction between the alcohols and acetic acid consists of reacting the two materials in either a continous process or batch type reactor in the presence of a small amount of sulfuric acid catalyst. This process is used to produce these acetates: ethyl, amyl, butyl, and isoproxyl as well as methyl salicylate, methyl anthranilate, diethyl phthalate, and dibutyl phthalate.

The esterification of acetylene is used to produce unsaturated vinyl type esters by addition of various organic or inorganic acids. Reactions are conducted in either the vapor or liquid phase. Products produced are vinyl acetate, vinyl chloride, acrylonitrile and vinyl fluoride. Yields are high, 80 to 95 percent, and polymerized reaction products are produced as solid wastes.

(10) Methanol

Methanol is produced principally by zinc oxide catalyzed air oxidation of methane at high temperature, and by reaction of hydrogen with carbon monoxide. The average amount of effluents from this process are (Reference 13):

Waste	lbs. /1,000 lbs. of Product
Free Floating Oils	0.17
Heavy Metals	
Chromium	0.01
Zinc	0.011
Organic Chlorides	0.18
Phosphates	0.004

(11) Ethylene Oxide

There are two processes for production of the very important intermediate, the chlorohydrin and the catalytic oxidation. Both use ethylene as the raw material.

The oldest process is the chlorohydrin which consists of reacting ethylene with hypochlorous acid with subsequent dehydrohalogenation with calcium hydroxide or sodium hydroxide. This process produces ethylene dichloride as a by-product in the ratio of 90:10 ethylene oxide to the dichloride. The process produces a calcium or sodium chloride solution, contaminated with the two products, as waste.

The catalytic process involves reaction of air (or oxygen) with ethylene over silver catalyst. Competing side reactions are combustion of ethylene and formation of a variety of polymerized fragments, and isomerization of ethylene oxide to acetaldehyde. Waste streams contain water, aldehydes and polymerization products or tars. Overall yields are about 60 percent.

4, DISPOSAL PRACTICES AND HAZARDS

The producers of the compounds discussed in this section are generally classified as being part of the petrochemical industry or the coal tar products industry. Many producers in these categories have totally integrated plants, particularly in the petrochemical field. A single producer is frequently concerned with producing almost all of the materials discussed. Consequently, a discussion of disposal practices for these two industries must include discussion of disposal practices for all materials covered here. To avoid redundancy and repetition,the entire discussion on disposal practices and hazards has therefore been incorporated into Appendix A-6.

INDUSTRIAL INORGANIC CHEMICALS

1. ECONOMIC STATISTICS

According to the 1967 Census of Manufactures (Reference 9), industrial inorganic chemicals industry can be classified as:

- SIC 2812—Alkalies and Chlorine
- SIC 2813—Industrial Gases
- SIC 2816—Inorganic Pigments
- SIC 2819—Industrial Inorganic Chemicals Not Elsewhere Classified.

(1) SIC 2812—Alkalies and Chlorine

This industry comprises establishments primarily engaged in manufacturing chlorine, sodium carbonate, sodium hydroxide, potassium hydroxide, and sodium bicarbonate. Relative size and distribution of this industry is indicated by the following data (Reference 9).

	Value Added (10^6 dollars)	Establishment	Employees (1,000)
Northeast Region	N. A.	5	N. A.
North Central Region	109.7	9	7.4
Southern Region	200.9	22	7.5
Western Region	N. A.	8	N. A.
Total United States	419.2	44	19.2

(2) SIC 2813—Industrial Gases

The products and the 1967 production quantity reported for this industry is as follows (Reference 9):

Product	Quantity	Units
Acetylene	14,200	mil. cu. ft.
Carbon Dioxide	1,089	1,000 short tons
Argon	1,912	mil. cu. ft.
Helium	4,712	mil. cu. ft.
Hydrogen	158,539	mil. cu. ft.
Nitrogen	103,933	mil. cu. ft.
Oxygen	225,191	mil. cu. ft.
Nitrous Oxide	953	million gals.

The geographic distribution is indicated by the number of establishments shown below:

	Number of Establishments with More Than 20 Employees
United States	156
North East Region	36
North Central Region	45
Southern Region	45
Western Region	30

(3) SIC 2816—Inorganic Pigments

This industry comprises establishments primarily engaged in manufacturing inorganic pigments such as black pigments (except carbon black), white pigments and color pigments. The organic color pigments are classified in SIC 2815. The products of this industry are:

- Titanium pigments
- White lead
- Zinc oxide pigments
- Zinc sulfide
- Chrome colors
- Chrome oxide green
- Chrome yellow and orange

- Zinc yellow
- Iron oxide pigments
- Red lead
- Litharge.

(4) SIC 2819—Industrial Inorganic Chemicals Not Elsewhere Classified

Important products of this industry include inorganic salts of sodium (excluding refined sodium chloride) potassium, aluminum, calcium, chromium, magnesium, mercury, nickel, silver, tin; inorganic compounds such as alums, calcium carbide, hydrogen peroxide phosphates, sodium silicate, ammonia compounds, anhydrous ammonia; rare earth metal salts and elemental bromine, fluorine, oidine, phosphorus, and alkali metals (sodium, potassium, lithium, etc.).

Production quantity data from Reference 9 is given below:

	1,000 short tons
Nitric Acid (100% HNO_3)	6,265
Ammonia (100%)	
Anhydrous	12,200
Aqua	65
Ammonium Nitrate (100%)	6,005
Ammonium Sulfate (100%)	2,079
Calcium Hypochlorite	40
Sulfuric Acid	28,815
Boric Acid	122
Chromic Acid	22

Hydrochloric Acid	1,630
Hydrocyanic Acid	126
Hydrofluoric Acid	183
Phosphoric Acid (100%)	5,066
Aluminum Oxide	6,046
Aluminum Chloride	60
Aluminum Hydroxide	276
Aluminum Sulfate (17% Al_2O_3)	1,101

The relative size and growth of this industrial sector is indicated by the following data (Reference 9):

	Establishments (20 or more employees)	Employees (thousands)	Value Added (Millions of $)
1967	358	81.2	2295.4
1963	323	82.4	1902.6
1958	301	89.9	1468.9

This industry is distributed throughout the country. The relative concentrations by states is indicated by the value added data shown on the following page:

	Establishments (20 or More Employees)	Value Added (Millions of $)	Region Totals
Massachusetts	5	11.9	
New York	11	42.9	Northeast
New Jersey	31	101.3	
Pennsylvania	19	86.0	245.5
Ohio	25	189.6	
Indiana	8	49.1	
Illinois	23	70.8	
Michigan	11	70.1	North
Minnesota	2	7.6	Central
Iowa	7	(D)	
Missouri	7	48.8	
Nebraska	6	(D)	
Kansas	5	49.8	551.6
Delaware	3	(D)	
Maryland	9	40.4	
Virginia	5	33.3	
North Carolina	4	(D)	
South Carolina	1	(D)	
Georgia	11	37.7	
Florida	11	31.2	
Kentucky	6	76.1	
Tennessee	17	322.9	
Alabama	4	(D)	
Mississippi	5	(D)	
Arkansas	7	72.1	South
Louisiana	16	121.6	
Oklahoma	4	1.8	
Texas	30	141.5	1149.5
Montana	2	(D)	
Idaho	3	103.4	
Colorado	4	6.5	
Nevada	2	(D)	West
Washington	5	(D)	
California	36	110.7	348.7

Because there is such a wide variety of products made within this sector, a limited number of process types have been selected for review on the basis of availability of data and their relative importance to hazardous waste problems.

2. WASTE CHARACTERISTICS

Waste streams from inorganic chemical manufacturing vary both quantitatively and qualitatively depending on the type of compound or compounds manufactured, processes used, and the raw materials used. In general, waste streams may be expected to contain variable amounts of dissolved and suspended solids in the form of acids, alkalies, troublesome and/or toxic chemicals such as fluorides, phosphates, sulfates, organic solvents, greases and lubricating oils, metals, and warm water and/or steam.

Waste waters often consist of both contaminated and relatively clean effluent streams. In general, contaminated waste waters are those taken from processes, while the cleaner waste waters are those used for the purpose of cooling, general washing,etc. Contaminated waters, on the other hand, result from filter ash washing, waste acid and alkalie streams, working and process streams. Process waters are segregated from cooling waters in many plants to reduce the volume of water which requires treatment prior to discharge.

Clean waste water streams, though basically uncontaminated may, however, produce adverse thermal effects such as decreased oxygen solubility, greater oxygen utilization, as well as a list of related problems, by virtue of their temperature.

Many processes utilized in the manufacture of inorganic chemicals generate large amounts of thermal energy which must be removed by cooling water or air. Of particular significance are the gas producing plants because of their need to discharge heat extracted fan air or natural gas during compression and subsequent cooling steps. Blow down from recirculating systems may also contain substantial amounts of chemicals added to the cooling water. These include chromates, zinc, phosphate, bactericides, and organic compounds, and may constitute pollution problems. The use of cooling towers may create ice fogs and other inadvertant weather modifications.

(1) Composition of Waste Streams

The composition of process waste streams is highly varient, the effluents and treatment procedures for a variety of manufacturing processes will be discussed. The effluents from any production complex are dependent on the products which are in production currently. A wide variation in waste composition and total waste is possible. To illustrate this point, effluents from two complex facilities (designated 1 and 2) are given in Table A-5-8 . Complex 1 manufactures sodium sulphate, sodium thiosulphate, and zinc sulphate. Effluents from this complex include sulphate, zinc, and sodium bicarbonate. Effluents from Complex 2 include chlorine, ammonia, iron, phenol, and large quantities of dissolved and suspended solids.

The discussions of individual processes which follow (Reference 2) should be viewed occurring in a separate facility or as one process in a plant producing several products. Most of the inorganic chemicals discussed are for the most part relatively innocuous. This does not mean that all plants which produce inorganic chemicals have relatively less hazardous wastes. Inorganic chemicals may be produced by plants which produce organic compounds which are highly toxic. In such cases waste streams may contain substantial amounts of potentially hazardous compounds.

1. Gases

Nitrogen, oxygen, and other gases are extracted from air by medium pressure liquification and rectification of air. Waste problems result from heated cooling water

Table A-5-8
Effluents from Two Complex Facilities

	Complex 1	Complex 2
Products of Complex	Sodium sulfite, sodium thiosulfate and zinc sulfate	Soda ash, sodium bicarbonate, chlorine, caustic soda, hydrochloric acid, sodium silicate, and calcium carbonate
Effluent Flow Rate (GPD)	300,000 for process 1,500,000 total	6,000,000 total
Effluent pH	6.5-8.5	11
$SO_3^=$(ppm)	20,000	--
Zn^{++}	20	
NaCl (ppm)	45,000	--
$NaHCO_3$ 9ppm)	15,000	--
Suspended solids (ppm)	--	30-50
Cl^- (ppm)	--	79,000
NH_3 (ppm)	--	4
Total soluble solids (ppm)	--	131,000
Fe, soluble (ppm)	--	0.36
Phenols (ppb)	--	219
Hardness, equiv. $CaCO_3$ (mg/l)	--	76,000

and from waste compressor oils. The quantity of such oil varies greatly from plant to plant depending on compressor type, size, and age. Oil emissions are controlled by skimming and/or biological treatment.

The wastes associated with typical inorganic chemical production processes are discussed in the paragraphs that follow. Table A-5-9 summarizes these product-processes, the significant wastes, and the treatment provided to reduce the hazards related to these wastes.

2. Inorganic Acids

Effluents from acid manufacturing plants range from a highly contaminated streams to relatively clean streams containing small amounts of waste acids. In the manufacture of hydrochloric acid (about 85 percent of which is obtained as a by-product of chlorination of hydrocarbons, waste streams consist primarily of HCl for which neutralization is the best available treatment method. The highly toxic organic contaminants such as chlorobenzene and phosgene are also found in the waste. In plants using the synthetic process, i.e., burning of hydrogen in chlorine gas, HCl waste effluents are often used to neutralize caustic effluent from adjacent or nearby chlor-alkali plants.

Table A-5-9
Raw Waste and Effluent Data for Inorganic Chemicals

Product/Process	Effluent (lbs/ton)	Treatment
HCl (Direct Burning)	HCl - 41	Use to neutralize caustic wastes
HNO_3 (Ammonia Oxidation)	HNO_3 - 6	Recycle wash water
H_2SO_4 (Contact)	H_2SO_4- 1.0	Neutralize with lime
	SO_2	Scrubber exit gases
HF (Reactor with Florspar)	$CaSO_4$ - 7100	Settling—water recycle
	CaF_2 - 120	Lime treatment—settling
	H_2SO_4 - 500	Neutralization and ponding
	Silica - 30	Settling pond
Phosphoric Acid (Wet Process)	$CaSO_4$ - 1580	Settling—water recycle
	CaF_2 - 68	Lime treatment—settling
	Phosphates - 45	Lime treatment—settling
	Silicates - 170	Settling
	Phosphoric Acid - 1	Reuse wash down water
Phosphoric Acid (Dry Process)	AS_2S_3 - 0.3	Scrubbers, collection, burial

Table A-5-9
Continued

Produce/Process	Effluent (lbs/ton)	Treatment
Phosphorus (Electric Furnace)	Phosphorous - 12	Settling — Burial
	Soluble - 11 phosphates	Lime treatment, settling - recycle water
	Fluorides - 8	Lime treatment, settling, recycle water
	Solid Phosphates - 115	Dry collection and reuse
Hydrogen Peroxide (Organic Solvent)	Organic Solvents - 4	Biodegradable - activated sludge
	H_2O_2 - 40	Recycle
Aluminum Chloride (Molten Aluminum)	$AlCl_3$ - 32	Wet alkaline scrubbing, settling
	Cl_2 - 8	Wet alkaline scrubbing, settling
	HCl - 8	Wet alkaline scrubbing, settling
Aluminum Sulfate (Wet Acid)	Silicates - 270	Lime neutralization, settling
	Aluminates - 75	Lime neutralization, settling
	H_2SO_4 - 10	Lime neutralization, settling
	Fe_2O_3 - 11	Lime neutralization, settling

Table A-5-9
Continued

Produce/Process	Effluent (lbs/ton)	Treatment
Ammonium Nitrate	None	None
Ammonium Sulfate (Ammonium Salts)	$CaCO_3$ - 1200	Settling pond

The typical effluents, amounts per ton of product and the typical treatment required are shown in Table A-5-9. This table gives data for a plant representing about 1 percent of the U.S. HCL production.

Waste sources in the manufacturing of nitric acid are confined typically to area wash down operations, cooling water blowdown, and samples taken for quality control. These small amounts of waste waters are collected and used as process water to make nitric acid in most facilities, and in general, there is no discharge of waste from a nitric acid plant during normal operations. Waste loads range from 0.1 to 1.0 pound of NHO_3 waste per ton of HNO_3 produced.

Sulfuric acid, mainly manufactured by the direct reaction of oxygen and sulfur, is also relatively pollution free. Since no process water is discharged from newer plants, the only pollution arises from cooling water treatment chemicals, spills and wash-downs. In most plants, the wash-down water is collected and reused to make sulfuric acid. In older facilities or spent acid plants, wash-down waters are currently treated with lime to neutralize the H_2SO_4.

By-product steam can be of economic value in some instances. To prevent thermal pollution, cooling ponds and towers are used.

Hydrofluoric acid is manufactured by the reaction of sulfuric acid with fluorspar (CaF_2). By-product gypsum is generally discarded. Effluents from HF plants include $CaSO_4$, CaF_2, H_2SO_4 metal oxides, silica, H_2SiF_6, and HF. The standard method of waste treatment consists of the addition of lime to neutralize the sulfuric acid, minimize fluoride content to 5 ppm and ponding to settle out the gypsum.

Eighty percent of the phosphoric acid manufactured in the U.S. is produced by acidulation of phosphate rock, while the remainder is made by burning phosphorous followed by hydrolizing the P_2O_5.

Sources of waste for the acidulation process include testings from phosphate rock benefication, and sludges of aluminum and iron phosphate. Scrubber waters contain large amounts of acid fluorides. The primary source of waste, however, is waste gypsum from acidulation. This semisolid waste may contain quantities of H_2SO_4 and phosphoric acid.

Wet processes phosphate and sulphate wastes are fairly constant, Those for fluoride and silica vary considerably due to differences in raw materials.

Current treatment of wastes from the acidulation process consists of settling in ponds to remove insoluble $CaSO_4$ (gypsum), CaF_2, and SO_2. This treatment is generally followed by two liming operations on ponds to percipitate soluble fluoride as CaF_2. In Florida, water from the ponds is recycled to the process. Water is discharged from ponds only during the rainy season. Other locations still discharge wastes from ponds directly into rivers.

The contribution of flurides to the product, gypsum, pond water and release to the atmosphere during phosphoric production processes are presented in Table A-5-10. As shown in the table (Reference 3), the fluoride emissions are directly proportional to the quantity of fluorides present in the phosphate rock.

Phosphoric acid waste from the dry process is not treated. Arsenic removed in the purification step is either buried in containers as AS_2S_3 or ponded. After neutralization to precipitate it as an insoluble compounds. No data is presently available on effluents leaving these ponds.

3. Phosphorous

Phosphorous is processed in electric furnaces by high temperature heating of phosphate rock, combined with sand and coke. Wastes include slag from the electric furnaces, dust waste from exhaust gas precipitation and phosphorous waters (knonw as "phossy" water) from dewatering processes. The data in Table A-5-11 are based on approximately 40 percent of the nation's production (some 610,000 tons in 1969).

Table A-5-10
Distribution of Fluorides from Phosphate Rock

lb/day F^-				
Input Rock	To H_3PO_4	To Gypsum	To Pond Water	To Atmosphere
73,600	21,500	30,000	21,200	12
116,300	28,000	39,000	48,500	30
355,600	105,900	75,100	174,600	24

Table A-5-11
Reaction of Gypsum Pond Water with Lime

$CaCO_3$ Charged (lb/1000 gal)	% of Theoretical	pH of Filtrate	Composition of Filtrate (g/liter)			
			P_2O_5	CaO	SO_4	F
0	--	1.8	2.00	1.40	2.76	2.90
43	50	3.2	1.65	1.20	2.50	1.00
67	75	3.4	1.41	1.10	2.30	0.07
90	100	4.8	0.59	1.10	2.60	0.02
100	110	5.1	0.58	1.10	2.70	0.02
112	125	5.1	0.58	1.10	2.60	0.03
133	150	5.1	0.58	1.10	2.60	0.03

Phosphorous contained in water streams is treated by clarification methods to settle out and recover some colloidal phosphorous. Residual water is either fed to an evaporation pit without discharge, pumped into a slag pile (which is ultimately buried), or recycled. For plants recycling their condemnation streams, the phosphorous content of the effluent is reduced to 0.05 ppm.

Burial is the best treatment currently in use for phosphorous settled from phossy streams. Treatment of the other process water streams generally consists of lime treatment to reduce fluoride and phosphate content and settling in ponds to remove insoluble materials. Water is then discharged, or may be recycled. Airborne solids collected by precipitation are generally recycled.

4. Hydrogen Peroxide

Hydrogen peroxide is made by either the electrolytic process or by an organic based process using anthraquinine dissolved in an organic solvent or liquid isopropylalcohol. The organic processes are of major importance. Waste streams include cooling water, extraction and purification water, and waste water from cleanup operations. These effluents contain sulfuric acid, H_2O_2 and organic solvents. Treatment is primarily confined to neutralization of the sulfuric acid and activated sludge treatments to remove the biodegradable solvents.

5. Calcium Carbide

Calcium carbide is manufactured by the reaction of quicklime (CAO) and coke in an arc furnace. No water is used in the process. Wastes result primarily from wet scrubbing of gaseous effluents and from the washdown of equipment. The waste steams from scrubbers and washdowns consist of lime and dissolved acetylene. 0.9 pounds of slaked lime/ton of CaC_2 is estimated to be produced.

6. Lime

Lime is manufactured by thermal decomposition of limestone of calcium carbonate in kilns. No process water is used so that the only waste results from wet scrubbing of the gaseous effluents to remove particulate matter. These effluents contain calcium carbonates and hydroxides and are slightly alkaline. At present, no treatment of scrubber waste is used; however, problems associated with wet scrubber effluent may be circumvented by the use of dry collection methods. The low waste load from lime plants is estimated to be ≈0.9 pounds of $CaCO_3$ plus CaO_2 pound of product.

7. Aluminum Chloride

Aluminum chloride is manufactured by chlorinating liquid aluminum. The process uses no water, hence all of the waste water comes from wet scrubbing of gaseous effluents (HCl, Cl, and HCl_3). Scrubbers in the aqueous phase may be made alkalie to increase efficiency, resulting in effluent containing Al salts, chlorides, and hypochlorides. In some plants there is no further treatment of scrubber efflents. Settling tanks may be used to remove aluminum salts.

8. Aluminum Sulfate

Aluminum sulfate is made by the reaction of dilute sulfuric acid with ground bauxite. The liquor is subquently treated with barium sulfide to precipitate iron.

9. Ammonium Nitrate

Ammonium nitrate is manufactured by reacting preheated ammonia and nitric acid and air drying the molten product in a cooling chamber. Wash-down procedures produce substantial amounts of nitrogen rich waste water. Additional waste quantities are obtained from scrubber blow downs, and from cooling water.

A potential hazard involved in the manufacture of NH_4NO_3 is the potentially violently explosive nature of concentrated solutions of NH_4NO_3 at high temperatures, especially if contaminated with organic material.

10. Ammonium Sulfate

About 35 percent of the ammonium sulfate produced is manufactured by the direct reaction of ammonium salts such as carbonates, with sulfuric acid. Some is made using gypsum in place of sulfuric acid. Major wastes involve solid discharges of by-product materials. The major amounts of ammonium sulfate are made during the recovery of ammonia from coke oven gas. About 40 percent of the total production is involved with the actual recovery of by-product ammonia from a variety of other processes.

3. DISPOSAL PROCESSES

A variety of treatment methods and processes are currently being used by manufacturers of inorganic chemicals (Reference 4) to control solid, liquid, and thermal wastes including:

- Chemical additon
- Equalization
- Sedimentation
- Filtration
- Reverse osmosis
- Electrodiolysis
- Ion exchange
- Multiple effect evaporation
- Deep well injection
- Ocean burial
- Dumping and landfill
- Lagooning/cooling ponds/solar evaporation ponds
- Centrifugation
- Cooling towers.

Three typical schemes are indicated in Figure A-5- for the treatment of (1) waste containing dissolved and suspended

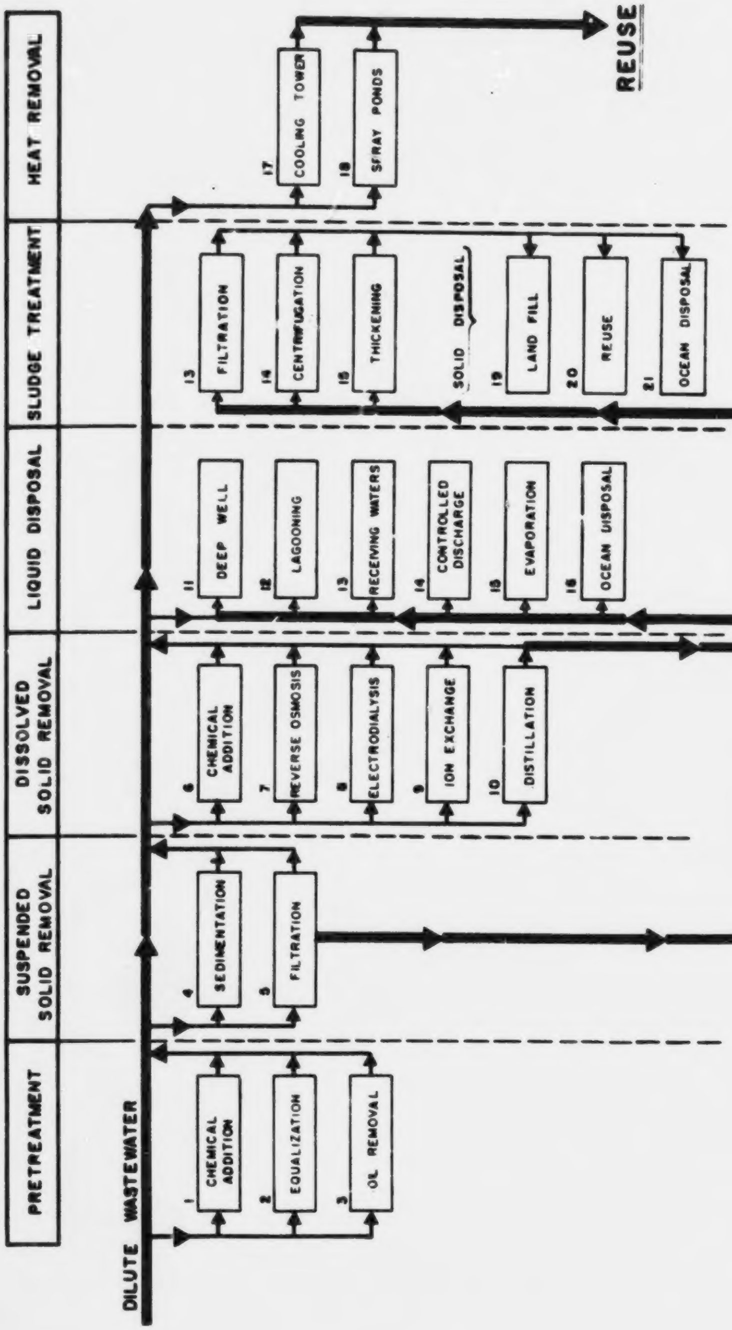
PRETREATMENT
SUSPENDED SOLID REMOVAL
DISSOLVED SOLID REMOVAL
LIQUID DISPOSAL
SLUDGE TREATMENT
HEAT REMOVAL
DILUTE WASTEWATER
1 CHEMICAL ADDITION
2 EQUALIZATION
3 OIL REMOVAL
4 SEDIMENTATION
5 FILTRATION
6 CHEMICAL ADDITION
7 REVERSE OSMOSIS
8 ELECTRODIALYSIS
9 ION EXCHANGE
10 DISTILLATION
11 DEEP WELL
12 LAGOONING
13 RECEIVING WATERS
14 CONTROLLED DISCHARGE
15 EVAPORATION
16 OCEAN DISPOSAL
13 FILTRATION
14 CENTRIFUGATION
15 THICKENING
SOLID DISPOSAL
19 LAND FILL
20 REUSE
21 OCEAN DISPOSAL
17 COOLING TOWER
18 SPRAY PONDS
REUSE

FIGURE 7
Wastewater Treatment Sequence

solids, (2) excess thermal energy discharge, and (3) waste containing primarily only dissolved solids respectively.

Where waste water contains appreciable dissolved and suspended solids, a typical treatment process might be 2-3-4-7-11-15 for liquids, and 15-14-12-17 for solids.

In this sequence, the waste flow is equalized, followed by oil removal. Clarification is used for suspended solids removal and the dissolved solids are concentrated and disposed of in deep wells. Effluent distillate is then discharge or reused. Suspended solids slurries are thickened, entrifuged, and lagooned. Alternately, chemical addition could be used for dissolved solids removal if the dissolved ions have a common insoluble salt. Dissolved solids may also be concentrated by electrodiolysis or ion exhcange instead of distillation. These may be recovered and/or converted to a marketable product.

Where there is excess thermal energy discharge, a treatment sequence might be 17-6-4-13. Here a cooling tower or pond would be used, and the cooled effluent reused or discharged. If the water is recycled, the blowdown from the system may be treated by chemical additon and clarification to remove undesirable components, especially CrVI and zinc added for corrosion control. Suspended matier would then go into a solid disposal sequence. In some cases, such as in the manufacture of H_2SO_4, by-product steam may be used to economic advantage.

Where there is a heavy dissolved solid load but a light suspended solid load, a sequence for acidic effluents would be 2-1-7-11-13. Here neutralization would occur after equalization, followed by reverse osmosis (or distillation, ion exchange or chemical addition), before alternate disposal such as deep well injection or evaporation to dryness.

In general, it is advantageous to keep contaminated and relatively clean effluent streams segregated, since most methods aim at concentrating effluents before discharge, or work better when solutions are more concentrated.

SIC 282 - PLASTIC MATERIALS AND SYNTHETIC RESINS, SYNTHETIC RUBBER, SYNTHETIC AND OTHER MAN-MADE FIBERS, EXCEPT GLASS

1. ECONOMIC STATISTICS

Production of all thermoplastic and thermosetting resins in the United States was 16 billion pounds in 1968, of which 12.3 billion pounds (over three-fourths of the total) represented thermoplastics. The statistics for all major resin types are shown in Table A-5-12. The aggregate growth rate of all thermoplastic resins is expected to level out at about 11 percent per year over the next decade, compared to an expected rate of about 5 percent per year for thermosets. Thus, thermoplastics will represent an even greater share of total resin production in the future.

Three types of thermoplastics—polyolefins (PO), polyvinyl chloride (PVC), and polystyrene (PS)—have experienced phenomenal growth, and should continue to do so. Polyolefins include both high- and low-density polyethylene (PE), and polypropylene (PP). The top position in thermoplastics is unquestionably held by polyethylene resins, whose 1968 production of 4.5 billion pounds was nearly twice

Table A-5-12

PRODUCTION STATISTICS FOR MAJOR RESIN TYPES

	1968 Production	
	Billions of Pounds	Percent of Total Resins
Polyethylene (low density)	3.3	21
Polyethylene (high density)	1.2	7
Polypropylene	0.9	6
Polystyrene (straight and rubber-modified)	1.8	11
Polyvinyl chloride	2.4	15
Cellulosics	0.2	1
Other thermoplastic resins	2.5	16
(Total thermoplastic resins)	(12.3)	(77)
Alkyd	0.6	4
Coumarone-indene	0.3	2
Epoxy	0.2	1
Phenolic	1.1	7
Polyester	0.6	4
Urea and melamine	0.7	4
Other thermosetting resins	0.2	1
(Total thermosetting resins)	(3.7)	(23)
Total resins	16.0	100

Source: U.S. Tariff Commission.

that of PVC, about two and a half times that of straight and rubber-modified PS, and about five times that of PP. Table A-5-13 shows the estimated distribution of major U.S. thermoplastics production capacity at the end of 1969.

Table A-5-13
Distribution of Production Capacity
For Large Volume Thermoplastic Resins

Polymer			U.S. Producers	U.S. Plants	Estimated Capacity End of 1969 (billion lb/yr)
PO	PE	LDPE	13	21	4.25
		HDPE	13	15	2.11
		PP	8	8	1.26
		PVC	23	35	3.72
		PS	15	30	2.54
					13.88

(1) Industry Descriptions

The industries included in this category are:

2821 Plastic Materials, Synthetic Resins - manufacturers of the resins, cellulose, and casein plastic—not the users of such materials.

2822 Synthetic Rubber - manufacturers of synthetic rubber by polymerization or copolymerization, but not the manufacturers who use such products to make final products.

2823 Cellulosic Man-Made Fibers - manufacturers of rayon and similar cellulose fibers.

2824 Synthetic Organic Fibers - manufacturers of all synthetic fibers other than cellulosic fibers, such as nylon, acrilon, etc.

(2) Establishment Size and Location

Production data for 1967 and 1958 are shown to illustrate the magnitude of this industry and its growth rate.

Industry (SIC Code)	Value Added (million $)		Establishments (20 or more employees)	
	1967	1958	1967	1958
2821	1635.1	872.0	340	196
2822	404.9	197.9	28	18
2823	506.8	390.3	20	26
2824	1251.8	439.6	35	14

The geographic spread of these industrial groups is shown by the following distribution table.

Division	Number of Establishments With Over 20 Employees Industry (SIC Code) 2821	2822	2823	2824
New England	49	-	1	-
Mid Atlantic	98	2	4	2
East North Central	69	4	1	-
West North Central	9	-	-	-
South Atlantic	36	3	7	27
East South Central	16	3	6	6
West South Central	18	14	-	-
Pacific	45	2	-	-
Total	340	28	19	35

A relatively small number of companies manufacture most of the synthetic rubber and man-made fibers. Resin manufacturing is somewhat more widely distributed. The data as of 1967 (Reference 1) is given below:

	Percent Accounted for by:			
Industry (SIC Code)	4 Largest Companies	8 Largest Companies	20 Largest Companies	50 Largest Companies
2821	27	43	64	86
2822	61	82	100	-
2823	86	99+	100	-
2824	84	94	100	-

The industrial chemical industries (2815 and 2818), the plastic materials industries (2821, 2822, 2823 and 2824), and the petroleum industry (2911) are interrelated. Similar products may be made in each group, while feed stocks, intermediates, and by-products may be interchanged. Some plastics are also made in the miscellaneous plastics products industry (3079). Table A-5-14 illustrates this relationship (Reference 1).

2. WASTE CHARACTERISTICS

The growth of plastic producting during the past ten years has continued at an annual rate of 12 to 16 percent. The following tabulation shows the effect of this growth rate on the production of the various types of plastics and resins.

Table A-5-14
Shipments by Product Class and Industry, 1967

Material	2821	2822	2823	2824	3079	2815 2818 2911
Plastic Film	190.1	-	-	-	792.4	243.0
Cellulosic, except rayon	234.0	-	-	-	(10-20)	(50-100)
Thermoplastic Resins	1391.0	(5-10)	-	-	(-2)	(500-1000)
Thermosetting Resins	450.8	-	-	-	(-2)	(50-100)
Synthetic Resin Protective Coating	223.4	-	-	-	2.2	60.9
Custom Resins	191.3	(-2)	-	-	(10-20)	26.6
Plastics & Resins (NCC)	56.9	-	-	-	2.5	8.1
Synthetic Rubber	(20-50)	814.4	-	-	-	(100-250)
Other Products	577.0	97.4	-	-	-	-
Industrial Organic Chemicals	169.6	(50-100)	(50-100)	(20-50)	-	x
Cyclic Intermediates	44.9	(10-20)	-	-	-	-
Industrial Inorganics	12.8	-	8.1	(10-20)	-	-
Miscellaneous Plastic Production	127.2	-	-	(10-20)	x	-
Cellulosic Fibers	-	-	(500-1000)	(50-100)	-	(-2)
Non-Cellulosic Fibers	-	-	(50-100)	1863.9	-	(10-20)
Surface Active Agents	18.1		(+2)			

Comparative Production Increases - SIC 2821
(millions of pounds)

	1968	1958
Polyethylene	5,445	708
Polyvinylchloride	2,635	689
Styrene	2,896	673
Phenolic and other tar acid resins	1,096	532
Phthalic alkyd & other alkyd resins	691	523
Coumarone-indene	348	286
Urea and Melamine	816	349
Cellulosic plastic	187	146
Polyester resins	615	96
Epoxy resins	157	47
All other	1,460	424
Total	16,346	4,473

(1) SIC 2821 - Plastic and Synthetic Resins

Production within this category can be broken down into various classes of plastics and resins. A 1967 study (Reference 1) divided the production processes into nine product areas:

Cellulosics
Vinyl Resins
Polystyrene Resins & Copolymers
Polyolefins
Acrylics
Alkyd & Polyester Resins
Urea & Melamine Resins
Phenolic Resins
Miscellaneous Resins.

The wastes associated with each of these categories (References 1 and 2) are summarized in Table A-5-15.

(2) SIC 2822 - Synthetic Rubber

The major synthetic rubbers produced include:

Butadiene - styrene copolymers, hot process
Butadiene - styrene copolymers, cold process
Butadiene - acrylonitrite copolymers
Butyl rubber
Neoprene
Silicone rubber
Hypalon.

The waste products from the first three compounds are similar and vary only because of the differences in raw materials. Wastes contain minor amounts of raw materials as well as soaps, catalysts, and modifiers.

Typical reaction products for Butadiene rubbers include: butadiene, styrene, lorol mercaptan, potassium persulfate,

Table A-5-15

Plastic and Resin Associated Wastes

SIC Code	Plastic or Resin	Type of Product	Type of Waste	Waste (lb)/ 1000 lb Prod.	Waste Water (Gal/lb Prod.)
28211	CELLULOSICS	Cellophane Acetate Sheets	Regenerated cellulose: Cellulose Sodium hydroxide Sulfuric acid Sodium sulfate Carbon bisulfide Bisodium sulfide Cellulose esters: Acetic acid Methylenedichloride Magnesium sulfate Acetic anhydride Sulfuric acid Cellulose acetate Mercury chloride Copper chloride	20	30
28212	VINYL RESINS	Flooring Wire and cable Sound recordings	Surface active agents Catalysts Unreacted products Phenol Sodium phenolate Sodium hydroxide Carbon tetrachloride Chloroform	15	1-2
28213	POLYSTYRENE RESINS AND COPOLYMERS	Extrusions Lightweight rigid foams	Peroxide catalysts Methyl or ethyl cellulose Polyacrylic acids Polyomy alcohol Monochlorodimethyl ether Methylal Starches Calcium carbonate Calcium phosphate	10	1.5
28214	POLYOLEFINS	Films and sheets Insection molding	Low pressure polymerization catalysts: Trialkyd Aluminum Hexavalent chromium oxide Titanium chloride Chromium nitrate Nickel salts Colorants Lubricants Stabilizers Solvents such as xylene	NA	NA

Table A-5-15
Continued

SIC Code	Plastic or Resin	Type of Product	Type of Waste	Waste (lb)/ 1000 lb Prod.	Waste Water (Gal/lb Prod.)
28215	ACRYLICS	Fibers Coatings	Acrylonitrile Acrylic polymer Acrylic acid Dimethylformamide Dimethylamine Formic acid Dimethylcarbonate Monomers: Vinyl acetate Vinyl chloride Styrene Isobutylene Acrylamide Vinyl pyridine Inorganic salts such as Zinc	15	0.13
28216	ALKYD AND POLYESTER RESINS	Coatings Rigid foams Adhesive	Maleic anhydride Fumaric acid Styrene Propylene glycol Diethylene glycol Phthalic anhydride Adipic acid Catalysts such as Benzoyl peroxide Dicumif peroxide Calcium hydroxide Barium hydroxide Vinyl silicones	6	2
28217	UREA AND MELAMINE RESINS	Textile and paper treating Bonding	Urea formaldehyde butanol Dicyanodiamide Thiourea Caustic	35	0.10
28218	PHENOLIC RESINS	Electric insulation Plywood	Phenol Phenol alcohol Calcium hydroxide Sulfuric acid Formaldehyde	30	0.10
28219	MISCELLANEOUS RESINS Polyeurathane Epoxy Silicones Nylon	Foams Glues, moldings Electrical equipment Textiles, carpeting			

soaps, sodium formaldehyde, sulfoxylate, ethylene diamine tetraacetic acid, acrylonitrile, plasticizers, carbon black, caustic.

Neoprene production involves acetylene conversion to monovinylacetylene utilizing reactions with hydrogen chloride in a cuprous chloride solution. Other chemicals involved include such compounds as sodium hydroxide, potassium persulfate, sulfur, resin.

Most silicone rubbers are derived from dimethyl dichlorosilane prepared by passing methylchloride over powdered silicone with copper catalysts. Di-tert-butyl peroxide or dicumyl peroxides are used for vulcanization.

Typical waste effluents include:

	Raw Waste (ppm)	Waste After Settlement (ppm)	Waste After Filtration (mg/L)
Suspended Solids	5000	1000	-
BOD	700	160	80
COD	10000	1750	600
PV	1200	400	160
Ammoniacal N	8	-	-
Oxidized N	35	-	-
Total Phosphate (as P)	218	-	-
Phosphate in Solution (as P)	15	-	-

soaps, sodium formaldehyde, sulfoxylate, ethylene diamine tetraacetic acid, acrylonitrile, plasticizers, carbon black, caustic.

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PV	1200	400	160
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Oxidized N	35	-	-
Total Phosphate (as P)	218	-	-
Phosphate in Solution (as P)	15	-	-

(3) SIC 2823 - Cellulosic Man-made Fibers

Cellulosic Man-made Fibers are rayon and acetate fibers made from cellulose, typically wood pulp which is reacted with sodium hydroxide, the intermediate aged, and then mixed with carbon disulfide. Titanium dioxide may be added to remove the shine from the viscose rayon. Dyes are added as desired. The fiber is then produced by ejecting the polymer through a die into a zinc sulfate-sulphuric acid solution. Another method uses cupra ammonium in an ammonia caustic solution to form the polymer. Cellulose acetate is made by mixing cellulose, treated with acetic acid, with a mixture of acetic acid and sulfuric acid.

Wastes include cellulose, rayon, sodium hydroxide, mercury, carbon disulfide, cellulose xanthate, dyes, titanium oxide, zinc sulfate, sulfuric acid, sodium sulfate, hypochlorite, copper sulfate, ammonia, and, for cellulose acetate, acetic anhydride, methylene chloride, magnesium sulfate, acetic acid.

The characteristics of the waste liquor flowing from a plant will vary according to the details of operation at each site, such as the particular type of cellulosic produced (rayon, cupra ammonium cellulose, cellulosic acetate).

(4) SIC 2824 Synthetic Organic Fibers

Noncellulosic fibers include fibers such as nylon, orlon, dacron, saran, and similar fibers made from polyamide polyester and alkyd resins. The wastes from these processes will vary and such wastes may become part of a larger waste stream which embodies other chemical process wastes from other operations at the same site.

The wastes for nylon include: hexamethylene adepamide, monodi- and hydroxycarboxylic acid, dicarboxy acids, cyclohexanol caprolactum, adipic acid, and adiponitrile. For acrylics, the wastes are dimethylamine, dimethyl formamide, formic acid, acrylonotrile, dimethyl ammonium,dimethyl carbonate, inorganic salts, ethylene cyandhydrin, hydroorganic acid, and zinc.

3. WASTE DISPOSAL PROCESSES

In general, the raw waste water from plants in the plastics and fiber industries contains principally organic contaminants. With few exceptions, these lend themselves to standard biological treatment for the purpose of pollution control. Since many of the plants in these industries operate in states or municipalities which currently regulate and monitor industrial effluents, considerable experience is available on the waste reduction treatments.

(1) Waste Treatment Processes

The following descriptions briefly summarize the waste treatment processes for the plastics and fiber industries (Reference 3).

1. Coagulation

Coagulation is used to remove colloidal suspended materials (i.e., non-settling particles in the range of 10^{-7} to 10^{-5} cm in diameter). Coagulants such as organic polyelectrolytes dissolve to form ions. These neutralize the repelling charges on the colloidal particles permitting them to agglomerate into larger particles which can be settled.

2. Aeration/Activated Sludge

Biological oxidation, through the use of micro-organisms, duplicates portions of the natural cycle existing in bodies of surface waters, yielding carbon dioxide and water. The treatment plant, therefore, reduces the oxygen demand of the waste water to a level which can be handled by the receiving stream.

The principal biological oxidation in use is the activated sludge process. This consists of a continuous system in which biological growths are mixed with the waste water and aerated. The activated sludge (consisting of bacteria, fungi, protozoa, etc.) is settleable and is separated from the treated water. Some of the settled material is recirculated for admixture with the raw waste.

The oxygen required to satisfy the demand of degradable organic matter may be supplied through mechanical means via surface agitation or submerged air sparging or diffusion.

3. Trickling Filter

A trickling filter is a packed bed of media (e. g., stone) covered with a layer of microbial slime (similar in composition to activated sludge) over which waste water is passed. As the thin water layer passes over the surfaces, the biodegradable material is oxidized. The term "filter" is a misnomer, because the removal of organic material is not accomplished with a filtering or straining operation.

4. Flotation

Flotation is used for the removal of suspended solids from wastes and for the separation and concentration of sludges. The waste flow or a portion of clarified effluent is pressurized to 40 to 60 psi in the presence of sufficient air to approach saturation. When this pressurized air-liquid mixture is released to atmospheric pressure in the flotation unit, minute air bubbles are released from solution. The sludge flocs and suspended solids are floated by these minute air bubbles, which attach themselves to, and become enmeshed in, the floc particles. The air-solids mixture rises to the surface, where it is skimmed off. The clarified liquid is removed from the bottom of the flotation unit. At this time a portion of the effluent may be recycled back to the pressure chamber. When flocculent sludges are to be clarified, pressurized recycle will usually yield a superior effluent quality since the flocs are not subjected to shearing stresses through the pumps and pressurizing system.

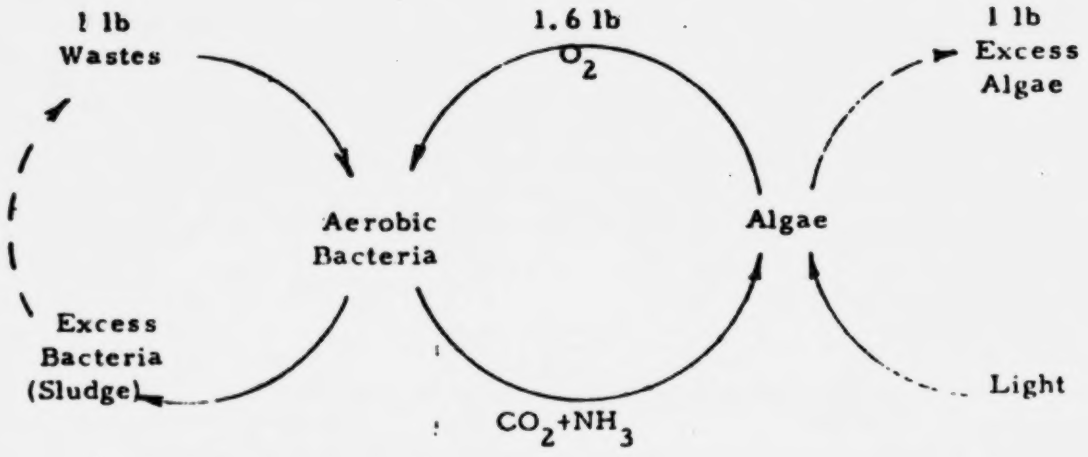
5. Sludge Handling

Sludges from activated sludge treatment frequently require concentration before they undergo further processing.

Settling ponds, mechanical thickeners or flotation equipment may be utilized. Normal sludges of 1 to 2 percent concentration can be thickened to 5 to 10 percent concentration. The thickened sludge can then be disposed of by various means: anaerobic digestion with the generation of methane and sulfides; dewatering of the raw or digested sludge with subsequent burning or use in land fill; wet combustion; or by conversion to protein for fertilizer or animal feed.

6. Lagoons and Stabilization Ponds

The fundamental principle underlying the most used types of stabilization ponds is that their action depends upon the simultaneous and continuous functioning of both sectors of the aerobic cycle of organic growth and decay. This contrasts with the conventional system which carries out only the degradation processes and leaves the growth potential to be exerted in the receiving water. The following drawing indicates the synergistic activity of bacteria and algae in photosynthetic oxygenation.


1 lb
Wastes
1.6 lb
O_2
1 lb
Excess
Algae
Aerobic
Bacteria
Algae
Excess
Bacteria
(Sludge)
CO_2+NH_3
Light

Significantly, although the system is internally self-sufficient, the input is biodegradable dead organic wastes, and the output is living organic matter at a higher energy level. The living algae cells, however, are not quickly available for biodegradation because of their tenacity of life. Nevertheless, in terms of water quality, the stabilization pond effluent may substitute an aesthetic factor for the quality factors associated with biodegradation unless algal cells are harvested.

Stabilization basins can be divided into two broad classifications: the impounding and absorption lagoon, and the flow-through lagoon. In the impounding and absorption lagoon there is no overflow or there is intermittent discharge during periods of high stream flow. The volumetric requirements of the basin must be equal to the total waste flow less losses due to evaporation and percolation. In view of the large area requirements, impounding lagoons are usually limited to industries discharging low daily volumes of wastes or to seasonal operations.

The flow-through lagoon can be classified into four categories depending on the nature of biological activity.

- Type I - Aerobic algae ponds. The aerobic algae pond depends upon algae to provide sufficient oxygen to satisfy the BOD applied to the pond. Since sunlight is essential to oxygen production by algae, the depth of the pond is limited to that through which light will penetrate. For most waste systems, this will not exceed 18 in.

  In order to maintain aerobic conditions in the settled sludge and to provide uniformity of oxygen, mixing of the basin contents for a few hours each day is essential. Separation fermentation. The depth of anaerobic ponds is selected to give a minimum surface area-to-volume ratio and, thereby, provide maximum heat retention.

- Type IV - Aerated lagoons. These lagoons have detention periods ranging from a few days to 2 weeks, depending on the BOD removal efficiency desired. Oxygen is supplied by diffused or mechanical aeration systems, which also cause sufficient mixing to induce a significant amount of surface aeration. Depths from 6 to 15 ft. are common.

In some industrial waste applications, aerobic ponds have been used after anaerobic ponds to provide a high degree of treatment. Stabilization basins are also used to "polish" effluents from biological treatment systems such as trickling filters and activated sludge.

7. Sedimentation

Settleable solids (particle size greater than 10^{-5} cm in diameter) are handled in lagoons or in clarifiers (thickeners). Lagoons must be periodically cleaned to remove the sediment. Clarifiers continually rake the solids to a center outlet where they are withdrawn.

An API separator is, in essence, a large-volume flow-through lagoon which permits free oils or low-density material to surface and be skimmed off. Similar lagoons are used in the plastics industry to remove lighter-than-water plastic particles by a partially submerged drag flight conveyor.

Three types of heavier-than-water sedimentation occur, depending upon the nature of the solids present: discrete, flocculent and zone settling. In discrete settling, the particle maintains its individuality and does not change in size, shape or density. Flocculent settling occurs when the particles agglomerate or coagulate during settling with a resultant change in size and settling rate. Zone settling involves a flocculated suspension which forms a lattice structure and settles as a mass, exhibiting a distinct interface.

8. Ion Exchange

Ion exchange, while normally used for influent water treatment, can also be useful for the removal of undesirable anions and cations from a waste water stream. Cations can be replaced by hydroxyl ions. The reactions which occur depend upon chemical equilibria situations in which one ion will selectively replace another on the ion exchange site. Cation exchange on a sodium cycle material can be illustrated by the following reaction:

$$Na_2 : R + Ca^{++} \longrightarrow Ca \cdot R + 2\ Na^{+}$$

where R represents the exchange resin.

When substantially all the exchange sites have been replaced with calcium, the resin must be regenerated by passing a concentrated sodium chloride solution through the bed. This reverses the equilibrium and replenishes the sodium content of the resin.

9. Oxidation-reduction and Precipitation.

Through the addition of suitable oxidating or reducing chemicals, soluble metal ions can be precipitated as the insoluble hydroxides and removed. pH control is usually required as well.

10. Adsorption.

Many industrial wastes contain organics in low concentrations which are difficult or impossible to remove by conventional biological treatment processes. These can frequently be removed by adsorption on activated carbon.

After the adsorptive capacity of the carbon has been reached, it is either replaced or regenerated by heating to desorb the separated impurity.

11. Reverse Osmosis.

Reverse osmosis is a technique being investigated for desalination of brackish water. It is also finding application in treatment selected industrial wastes.

(2) Waste Treatment Practices.

A wastewater treatment sequence is identified for these products, as reported by the participating manufacturers to the Celanese Research Company (Reference 4).

Obviously, the treatment sequence does not present the entire picture. With similar biological treatment, differ recovery efficiencies are achieved. A perfectly feasible treatment plant may be hydraulically overloaded with insufficient holdup time. Proper and adequate design is as important as the selection of treatment sequence.

For a stream which has undergone biological treatment, the suspended solids content of the effluent has no relation to the process. Since solids are created by the biological process, the suspended solids content of the effluent merely reflects the efficiency of the polishing lagoon.

Although there are a wide variety of plastics and synthetic fibers manufactured by various processes and techniques, the quality of the raw waste water streams can be classified into four general categories:

- Manufacturing processes that do not normally involve direct contact of water with the ingredients nor contribute pollution in any form to the water used
- Manufacturing processes in which the raw waste water has a very low BOD_5, a low-to-intermediate COD and a relatively low suspended solids content

- Processes in which the raw waste water has a high BOD_5, a high, but also completely degradable, COD, and relatively high suspended solids content, and

- Raw waste water of moderate BOD_5, moderate COD, low-to-intermediate suspended solids content but specific problems related to the rate of biological degradation.

Toxic or malodorous chemicals used in the manufacture of plastic resins or synthetic fibers normally are either recovered or chemically treated to the extent that they are not allowed to reach the receiving waters. For each raw waste water classification, the current usual treatment procedures are shown below:

Class I

28212 20	Polyvinyl Acetate Resin
28219 30	Urethane Resins
28245 10	Polyolefin Fibers

General Waste Water Characteristics: Either no water is used in the process or the waste water contains virtually no pollutants.

Usual Treatment: None required. Provision is usually made for handling leakage of process materials into cooling water.

Class II

28214 11	High-Density Polyethylene (HDPE) Resin
28214 12	Low-Density Polyethylene (LDPE) Resin

General Waste Water Characteristics: Very low BOD_5, low-to-intermediate COD, low suspended solids.

Usual Treatment: API separator (with or without filtration or drag conveyor to remove oily waste or polymer particles).

Class III

28211	Cellulosic Resins
28211	Cellophane
28214	Polypropylene Resin
28231	Cellulose Acetate Fibers
28232	Rayon Fibers

General Waste Water Characteristics: Intermediate-to-high BOD_5, COD and suspended solids. Rayon and cellophane process wastewaters contain high sulfates, and rayon process wastewater contains zinc.

Usual Treatment: Preliminary settling lagoon followed by aeration/activated sludge treatments (AS-Activated Sludge, AL-Aerated Lagoons, EA-Extended Aeration, and TF-Trickling Filter) and clarification. BOD_5 and COD reductions are generally high (80-95 percent). Sulfates are generally not removed. Zinc is precipitated as the hydroxide where State regulations mandate.

Essentially all of the COD is biodegradable under normal sewage conditions. Consequently, adequate sludge holdup time and extended detention time in polishing lagoons would allow for more complete biological degradation. Algae growth, however, could lead to rapid eutrophication. Algae harvest for either land fill or conversion to protein feed would be mandated.

Sulfate removal is considered uneconomical and not a serious pollution problem. Zinc removal processes are under development by two companies, American Enka and FMC's American Viscose Division. Removal of up to 98% of the zinc is possible.

Class IV

28211 10	Polyvinyl Chloride Resin
28212 30	Polyvinyl Alcohol Resin
28213 10	Polystyrene

28213 20	ABS, SAN Resins
28218	Phenolic Resins
28218	Epoxy Resins
28219 10	Polyacetal Resins
28219 40	Nylon Resins
28241	Nylon Fibers
28243	Acrylic Fibers
28244	Polyester Fibers

General Waste Water Characteristics: Intermediate-to-high BOD_5 and COD not readily degradable, low-to-intermediate suspended solids.

Usual Treatment: Preliminary settling lagoon (with or without neutralization) followed by aeration/activated sludge treatments (AS, AL, EA, TF) and clarification. Problem metals are generally coagulated and settled in a separate pond. Reduction or precipitation units may be used to reclaim zinc, antimony, or chromium. Absorption units may be used to eliminate toxic or malodorous chemicals from certain waste water streams. BOD_5 reduction is generally high (80-95 percent), and COD reduction is generally good (40-90 percent). Most of the BOD_5 and/or COD is generally biodegradable, but under non-normal sewage conditions. Some of the special problems which exist in the manufacture of this class of products are outlined below:

28212 10 Polyvinyl Chloride Resin

The raw waste water could contain some emulsion which usually requires a chemical coagulation step.

28212 30 Polyvinyl Alcohol Resin

Polyvinyl alcohol is extremely inert to biological degradation. Under the severe oxidation conditions of the COD analysis, it does show a COD value, but it would not be expected to degrade in a natural environment.

28218 Phenolic Resins

Phenol which might get into the raw waste water could present a taste problem if allowed to go out in the effluent. It is usually removed by an activated carbon absorption or an exchange process prior to activated sludge treatment.

28218 Epoxy Resins

An appreciable quantity of salt (NaCl) is evolved in the production of epoxy resins. It is not a toxic material and is usually not removed depending on the receiving water. If removal is necessary, a solid waste disposal problem would be created.

28213 10	Polystyrene Resin
28213 20	ABS, SAN Resins
28219 10	Polyacetal Resins
28219 40	Nylon Resins
28241	Nylon Fibers
28243	Acrylic Fibers

Principal contributors to process waste water for these products are monomers such as styrene, formaldehyde, caprolactam, hexamethylene diamine, adipic acid, low molecular weight polymers and sizing. These are biodegradable, but have a gestation time for initial biological attack that is longer than for normal sewage. These are referred to as "refractory" organics. Extended detention time in biological treatment ponds and polishing lagoons will allow for more complete degradation. For these materials, BOD_5 may not be too significant a parameter. Titanium pigments (TiO_2) used in most nylon textile compositions and the halogenated flame retardents used in acrylic carpets may also be found in the processing wastes.

28244 Polyester Fibers

A heavy metal catalyst is used in the manufacture of polyester fibers. The process waste water is consequently treated in a reduction unit, prior to biological treatment. This is primarily for recovery of a valuable material but also accomplishes pollution control. Complete removal of BOD material is not possible, even after long periods of aeration, because anto-oxidation of the sludge results in resolubilization of cellular material which is subsequently used for synthesis. Therefore, assuming optimum pH and temperature, adequate oxygen and nitrogen and phosphate nutrients, a removal efficiency of about 95 percent is theoretically possible.

Field confirmation of data will require close cooperation of the manufacturers. In many cases, raw waste water from the plant is not treated by itself. Usually, raw waste water streams from several process units are combined and treated together.

Polymer solid waste disposal practices presently employed by the plastics industry were reportedly limited to three: open dumping, sanitary landfill, and incineration. Resin producers who have relatively concentrated sources of polymer wastes typically handled their own waste disposal on company land. By contrast, plastics processors and fabricators (representing a much larger number of individual plants, with correspondingly less waste per plant) typically depended on public agencies or private contractors for their waste disposal.

SIC 283—DRUGS

1. ECONOMIC STATISTICS

(1) Description and SIC Classification

The term "drug industry" describes that segment of the manufacturing sector that produces chemicals, pharmaceutical products and biological and botanical products used for medicinal purposes. Between 2,000 and 3,000 companies are engaged in the manufacture of the variety of drug products available.

The Standard Industrial Classification (SIC) Manual defines the categories of drug manufacturers using the following four-digit numbers:

SIC 2831 — Biological Products
SIC 2833 — Medicinal Chemicals and Botanical Products
SIC 2834 — Pharmaceutical Preparations.

The assignment of these three industry codes is based on the following definitions:

SIC 2831—Biological Products: Companies primarily engaged in the production of bacterial and cirus vaccines, toxoids and analagous products (i.e., allergenic extracts), serums, plasmas, and other blood derivatives for human or veterinary use.

SIC 2833—Medicinal Chemicals and Botanical Products: Companies primarily engaged in (1) manufacturing bulk organic and inorganic chemicals and their derivatives, and (2) processing (grading, grinding, and milling) bulk botanical drugs and herbs. Establishments engaged in manufacturing agar-agar and similar products of natural origin, endocrine products, manufacturing or isolating basic vitamins, and isolating active medicinal principals such as alkaloids from drugs and herbs is also included in this industry.

SIC 2834—Pharmaceutical Preparations: Companies primarily engaged in manufacturing, fabricating or processing drugs into pharmaceutical preparations for human or veterinary use. The greater part of the products of these establishments is finished in the form intended for final consumption such as ampoules, tablets, capsules, ointments, medicinal powders, solutions and suspensions. Products of this industry consist of two important lines, namely: (1) pharmaceutical preparations promoted primarily to the dental, medical, or veterinary professions, and (2) pharmaceutical preparations promoted primarily to the public.

(2) Number of Establishments and Relative Concentration

The (1967) Census of Manufacturers (Reference 9) totals 1,129 establishments as primary producers within SIC Codes 2831, 2833, and 2834. The relationship between SIC code and numbers of establishments is as follows:

SIC	Number of Companies
2831	128
2833	126
2834	875

This tabulation does not account for companies producing products within more than one SIC category and is not an accurate indication of size of the drug industry. The total number of drug-producing companies is approximately 2,900, with 2,059 of these producing products in more than one of the three SIC codes (Tables A-5-16 and A-5-17). Companies producing products within more than one SIC code were listed only once. Manufacturing companies are operating in 47 States and the District of Columbia.

Table A-5-16
Geographical Distribution of Drug Industries

	Number of Establishments in Region *									
	A	B	C	D	E	F	G	H	I	Total
SIC 2831, -33, -34	105	712	189	387	57	128	192	32	257	2059
Unknown SIC	57	292	100	141	38	46	66	15	75	830
Total Drug Industries	162	1004	289	528	95	174	258	47	332	2889

	Percent in Region								
	A	B	C	D	E	F	G	H	I
SIC 2831, -33, -34	5.1	34.6	9.2	18.8	2.8	6.2	9.3	1.5	12.5
Unknown SIC	6.9	35.2	12.0	17.0	4.6	5.5	8.0	1.8	9.0
Total Drug Industries	5.6	34.8	10.0	18.3	3.3	6.0	8.9	1.6	11.5

*Regions are defined as follows:

A.	New England	F.	West South Central
B.	Middle Atlantic	G.	West North Central
C.	South Atlantic	H.	Mountain
D.	East North Central	I.	Pacific
E.	East South Central		

Table A-5-17
Percent in Five Top Drug-Producing States

	New York	California	New Jersey	Illinois	Pennsylvania
SIC 2831, -33, -34	17.4	10.8	10.5	8.5	6.6
Unkown SIC	21.7	7.7	6.5	6.4	7.0
Total Drug Industries	18.7	9.9	9.4	7.9	6.7

Geographic Area	Number of Companies SIC Code 2831	2833	2834
Northeast Region	30	51	326
North Central Region	44	35	262
South Region	30	20	170
West Region	24	20	117
Total (United States)	128	126	875

The percentage distribution of companies in those states having the largest number of companies is as follows:

	Number (Percent) Drug Companies				
SIC Code	New York	Calif.	New Jersey	Illinois	Penns.
2831	10(7.8)	15(11.7)	9(7)	6(4.7)	6(4.7)
2833	18(14.3)	16(12.7)	21(16.7)	13(10.3)	9(7.1)
2834	137(15.7)	90(10.3)	75(8.6)	72(8.2)	66(7.5)

(3) Major Raw Materials and Annual Production

The drug industry spans the numerous and varied operations required to produce a packaged product suitable for administration as a finished, usable medication. The conversion of raw materials to finished dosage form is concentrated in companies included in SIC Code 2384. Companies included in SIC Codes 2831 and 2833 may restrict production processes to those required for the manufacture of biological, botanical, or fine chemical substances for bulk distribution or may extend the scope of operation to include the conversion of these drug principals to a finished dosage form.

Industry processes begin with biological, botanical extraction, or chemical synthesis. Further processing includes milling, grinding, addition and mixing of excipients suited to the preparation of the final dosage form, depending upon the manufacturer's product requirement. Products and processes are briefly summarized as follows:

SIC 2831—Biological Products. Seed cultures (bacterial or fungal) are innoculated into a suitable medium which is then permitted to ferment. At the conclusion of the fermentation process, the bacterial and fungal solids are extracted from the ferment and discarded. The desired biological or chemical product is then purified. The purified product is then readied for bulk distribution or conversion by the manufacturer into a suitable dosage form.

SIC 2833—Medicinal Chemicals and Botanical Products. Products manufactured by companies included in this SIC code may have as starting materials animal tissues, botanicals, or synthetic raw materials. Fine chemicals are derived from animal or botanical sources using suitable grinding, extraction, and purification procedures. Fine chemicals are also produced from synthetic raw materials using appropriate chemical processing techniques. The derived products may be sold in bulk or processed by the manufacturer into suitable, finished dosage forms.

SIC 2834—Pharmaceutical Preparations. Active drug principals are converted into a variety of dosage forms. These include:

- Formulations for oral administration
  - Tablets
  - Capsules
  - Liquids
- Formulations for parenteral administration
  - Liquids
  - Pellets
- Formulations for topical administration
  - Liquids
  - Ointments
  - Aerosols

Raw material requirements for these varied operations, although numerous, can be conveniently described as follows:

- Basic active principals including substances derived from biological, botanical, or synthetic raw material sources
- Solvents and a variety of process chemicals
- Excipient materials including gelatin, starch, lactose, talcum, emulsifiers, coating materials, flavors, perfumes, and dyes
- Packaging items including:
  - Glass as bottles, vials, and ampoules
  - Plastic as vials, tubes, bottle caps, unit packaging
  - Metal as tubes, unit seals for parenteral containers and aerosol cans
  - Cardboard for unit containers and shipping cartons
  - Paper for labels, package inserts, and promotional literature.

One highly specialized area of pharmaceutical manufacturing is the preparation of radiological products. The processing of radioactive substances into pharmaceutical products is restricted to a very few companies. Although such products are used chiefly as diagnostic agents, there are a limited number of palliative products manufactured. The unique raw materials for this product group are the radionuclides incorporated into the desired dosage form (chiefly parenteral) and the specialized shielded (lead) packaging required for distribution.

The cost of materials utilized by companies included in the three SIC codes is shown in the following summary:

SIC Code	Number of Companies	Cost of Materials (10^6 dollars)	Delivered Cost (10^6 dollars)
2831	128	56.4	46.7
2833	126	206.1	-
2834	875	1,013.7	902.8

Total annual production of the drug industry ranges between single batch preparation of a few items to continuous processing of a large number of products. The value of product shipments taken from the Bureau of Census statistics (1967) for companies in the three SIC codes is shown in the following summary:

SIC Code	Number of Companies	Value of Shipments (10^6 dollars)
2831	128	160.0
2833	126	445.2
2834	875	4,696.4
Total	1,129	5,301.6

(4) Employment and Annual Sales

Although in excess of 2,000 companies are engaged in the production of drug products, approximately 95 percent of domestic ethical drug sales of dosage form products is attributed to 33 companies.

The global sales of United States pharmaceutical firms totaled 6.2 billion dollars in 1969. (Table A-5-18, which gives the sales according to various channels of distribution, was excerpted from Reference 13.) Of the domestic human-use product volume (4.03 billion), prescription legend drugs constituted 85 percent, with the remaining 15 percent resulting from sales of "over-the-counter ethical" products.

To accomplish this total dollar volume, global employment by the pharmaceutical industry totaled 230,900 people in 1969. Increases in numbers of employees by domestic-based and foreign-based firms contributed to a 1. 6 percent increase in total employment. In spite of the fact that some domestic firms reported decreases in employment, at least 14 firms reported employment in excess of 5,000 people, and included six companies employing 15,000 or more persons. Approximately 35 firms have 1,000 or more employees in ethical pharmaceutical

Table A-5-18

Ethical Pharmaceutical Sales[1]

Domestic and Foreign and Shares of End-Use Totals, 1969

(millions of dollars)

	Sector Destination							
	Domestic U.S. Sales			Foreign Sales				
Product Form and End Use	Private Sector	Govern-ments	Total Domestic Sales	Sales for Export to Other Firms	Sales Abroad[2]	Total Foreign Sales	TOTAL	Sales for Export Intra-Firm Trans-actions[3]
Dosage Form:								
Human Use	$3.689.9	$318.2	$4,008.1	$65.4	$1,552.6	$1,618.0	$5,626.1	$ 67.2
	65.6%	*5.6%*	*71.2%*	*1.2%*	*27.6%*	*28.8%*	*100.0%*	
Dosage Form:								
Veterinary Use	109.9	.7	110.6	1.2	94.5	95.7	206.3	8.7
	53.3%	*.3%*	*53.6%*	*.6%*	*45.8%*	*46.4%*	*100.0%*	
Bulk:								
Human Use	126.0	.8	126.8	22.0	62.3	84.3	211.1	115.6
	59.7%	*.4%*	*60.1%*	*10.4%*	*29.5%*	*39.9%*	*100.0%*	
Bulk:								
Veterinary Use	105.7	.1	105.8	3.1	55.7	58.8	164.6	14.1
	64.2%	*.1%*	*64.3%*	*1.9%*	*33.8%*	*35.7%*	*100.0%*	
TOTALS	**$4,031.5**	**$319.8**	**$4,351.3**	**$91.7**	**$1,765.1**	**$1,856.8**	**$6,208.1**	**$205.6**
	64.9%	*5.2%*	*70.1%*	*1.5%*	*28.4%*	*29.9%*	*100.0%*	

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[1] "Sales" are before deducting cash discounts and other marketing expenses, but after returns and allowances (domestic returns and allowances totaled $93.2 million in 1969). Export sales are f.o.b. U.S. port. A large majority of the firms reported most domestic U.S. sales were made f.o.b. purchaser's location or equivalent. The above domestic U.S. dosage form sales to the private sector are "gross" at invoice price. For "f.o.b. manufacturer's plant" totals, deduct $126.5 million ($64.4 million transportation out and $62.1 million company branch or field warehousing).

[2] "Sales Abroad" refers to sales in a foreign area by subsidiary or other corporate operations and excludes U.S. export sales. Excluded also are sales outside the U.S. by foreign-owned firms which have subsidiaries in the U.S. as PMA member firms.

[3] "Sales for Export (intra-firm transactions)" are sales to own International Division or for export to subsidiary abroad and are included as part of cost in "Sales Abroad.' Addition of the two "Sales for Export" columns will provide the aggregate ethical pharmaceutical exports reported by PMA member firms.

operations. These figures do not necessarily account for employees engaged in the manufacture of "proprietary" drug products.

Although sales are somewhat concentrated within a restricted number of companies, the industry is not dominated by any one company. The largest company share of domestic sales is approximately 7 percent with the 10 largest firms accounting for 52 percent of the total domestic market.

(5) Growth Patterns

Sales of ethical pharmaceuticals were expected to reach 7.0 billion dollars by the end of 1970. Exact figures are not yet available. An increase of 405 million dollars in domestic sales was forecast for the same period. The industry forecast of total sales suggested a growth rate of 13 percent compared to the actual 1968-1969 increase of 9.6 percent. In excess of 50 percent of companies, for which figures were available, anticipated an advance of 10 percent or more. Four percent of the companies forecast an anticipated growth rate of less than 5 percent. No company anticipated a decline in total sales.

Thus, based upon sales forecasts of 1970 sales, a 12.6 percent increase in ethical pharmaceutical sales over that figure recorded for 1969 global sales is anticipated. An increase of 9 percent is anticipated in domestic sales. Foreign sales are expected to increase approximately 11 percent.

The pattern of distribution remains relatively unchanged. Approximately 19 percent of direct sales are to hospitals with the remainder distributed to wholesale and retail channels.

2. WASTE CHARACTERISTICS

(1) Description of Production Processes and Waste Sources

The solid waste categories common to the majority of industrial codes are to be found in the drug industry. The potential problems of the drug industry, particularly those identified with the largest companies, parallel those associated with the chemical industry. Coupled with the chemical and packaging waste problems, are those wastes originating from biological, fermentation, botanical and radiopharmaceutical manufacture and process operations. Identification of the types of waste materials encountered is presented below. Since there is a wide variation in types of manufacturing in any one plant, not all wastes are necessarily found in each plant.

Paper
Cardboard
Plastic
Rubber
Glass
Metal
Dusts
Biological Tissue
Botanical Residues
Ashes

Waste Chemicals
Off-quality Products
Fermentation Solids
Acid and Alkali Sludges
Sewage Sludge
General Construction Trash
Cafeteria Wastes
Radioactive Wastes
Mixed Production Wastes (unidentified)
Production Solids (undifferentiated)

The potential for waste-product generation exists at all manufacturing and processing steps. In addition to biological raw material requirements of the industry, research utilization of animals is great; waste products generation in the category is greater than that found in most other SIC Codes. In addition, extensive chemical and microbiological research has the potential of generating waste products which may be accompanied by special disposal problems unique to the research activities.

1. Waste Generation During Process and Production

SIC 2831— Biological Products. Bacterial and fungal solids extracted from fermentation tanks are generally discarded as solid wastes. Spent broth and fermentation cakes also are wastes requiring disposal.

SIC 2831—Medicinal Chemicals. Chemical extraction of animal tissue results in solvent waste and spent animal tissue. The production of synthetic chemicals results in solvent waste and chemical solid waste.

SIC 2833—Botanical Products. Botanical products are manufactured by the extraction and purification of fine chemicals from botanical materials. The process results in both solvent wastes and solid waste consisting of bark, leaves, stems, and pulp.

SIC 2834—Pharmaceutical Preparations. Chemicals are weighed, mixed and channeled into one or more final dosage forms. These processes result in the generation of dusts, concentrated tailings, clean-up residues, off-quality products and returned goods as wastes. The specific composition of such wastes varies directly with the product involved and consequently such wastes are impossible to define in terms of specific material content.

2. Description of Effluents to Air and Water

Effluents to air do not appear to be a problem with the average small pharmaceutical plant but is more likely to be the problem of the larger companies. Potentially greater problems occur within those pharmaceutical manufacturers operating fermentation plants required for the production of antibiotics, steroids, and other products of biological origin. These problems are discussed in the rest of this section.

Dusts are also of great concern to companies within the industry. Dust inside a plant may result in "cross-contamination" of products. This is of major concern since there are some materials that are capable of producing extremely toxic reactions to some individuals when present in minute quantities (i.e., penicillin). This, coupled with the fact that manufacturers within the drug industry are extremely sensitive regarding their public image, has resulted in their taking all steps necessary to minimize the discharge of potentially noxious materials (including odor) into the air.

Fermentation is an important production process and represents the basic process for antibiotics and steroids. The most troublesome waste of the process and the one most likely to be involved in waste-water problems is "spent beer". This is the fermented broth from which the desired product has been extracted and contains a large amount of organic material, protein and other nutrients. The direct discharge of such a material into a stream or other body of water without eliminating or reducing the quantity of these materials can result in serious problems.

Spills of liquid and solid chemicals and solvents, both inside the production area as well as in general plant areas frequently occur and present an effluent water problem. Spills are washed down the nearest drain in order to quickly and conveniently clean the area involved. Thus, a potentially hazardous waste may be introduced into a storm sewer providing the most convenient drain was a storm sewer opening.

3. Hazardous Materials in Wastes

Enumeration of all potentially hazardous materials which appear as wastes generated by the drug industry is impossible. However, a grouping by descriptive class is informative. A summary by waste categories follows:

Group	Use	Wastes
Fine Chemicals (toxic)	Active ingredients in pharmaceutical formulations	Process dusts; off quality products returned goods
Synthetic raw materials (toxic)	Production of drug ingredients	Process dust; product tailings; off-quality products
Solvents (toxic - flammable)	Extraction and purification	Product tailings from recycling process; may be disposed of if recycling is not feasible
Radioactive wastes (toxic, radioactive hazard)	Preparation of radio pharmaceuticals; research	Tailings; product rejects
Animal wastes (pathogenic)	Production of biologicals; research needs	Tissues; carcasses; manure
Syringes and needles (accident hazard, reuse)	Research; product forms	As such
Biological wastes (bacteria, fungi, etc.)	Production; research	Spent broth; ferment cakes; residues
Glass (accident hazard)	Packaging; research	As such

The desirability of identification of the specific substances included as fine chemicals, synthetic raw materials, solvents and radioactive wastes is obvious. However, the number of chemicals involved coupled with changes in product type and process operation and the reluctance of manufacturers to disclose the nature of the processes used make it impossible to obtain a detailed inventory.

3. DISPOSAL PRACTICES

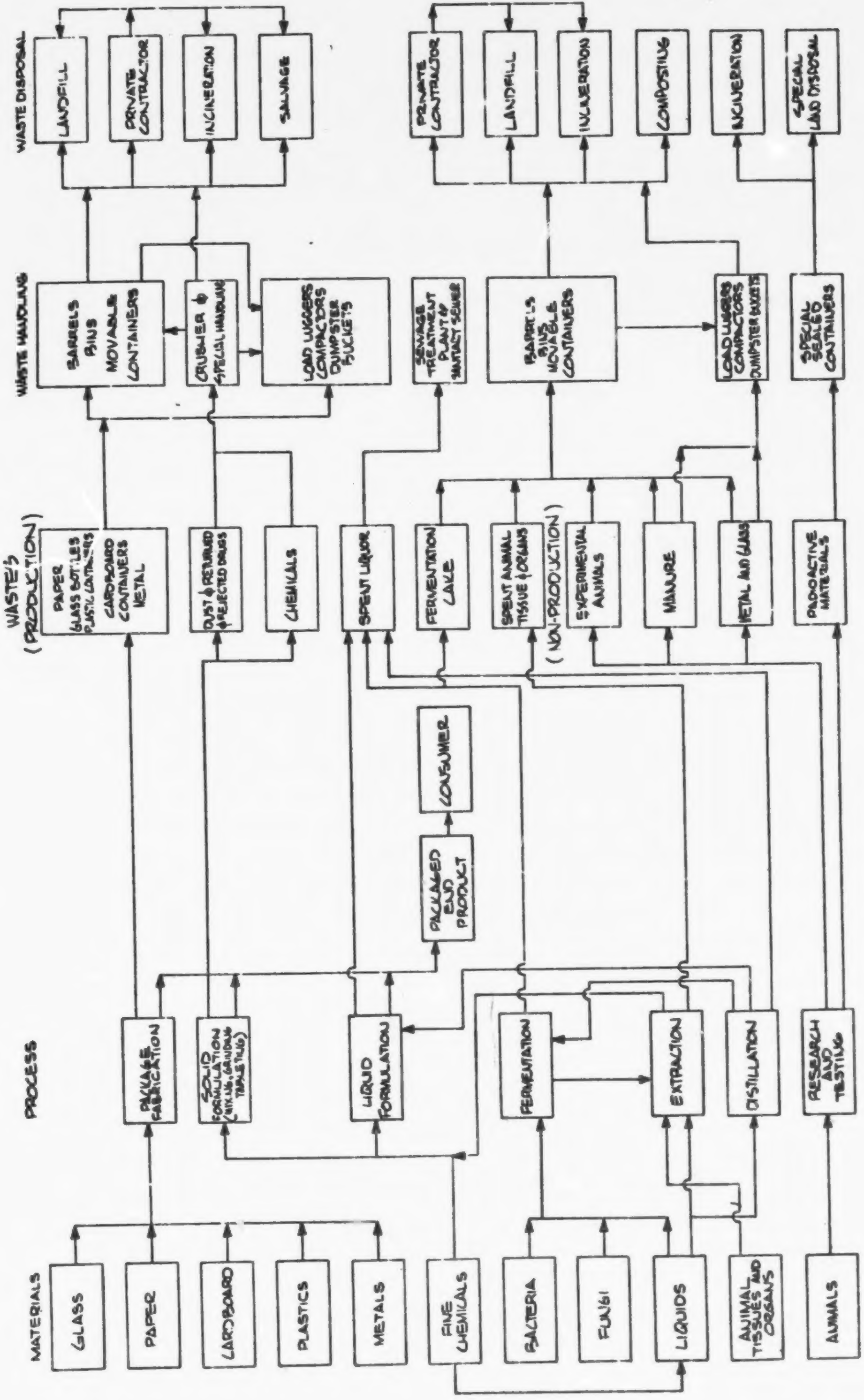
(1) Current Disposal Technology

The techniques used by the drug industry in handling process wastes and the methods of solid waste disposal are generally similar to those utilized in other industries and by municipalities (Reference 2). Figure A-5-8 summarizes the disposal practices for a number of companies regionally distributed throughout the U.S.

1. Solid Wastes

Movable containers are used to collect solid wastes at the source and to transport them to one or more general collection points. Frequent collections are then made from the collection point either by contract services or using company-owned trucks. Land disposal sites, either privately

FIGURE A-5-8
Flow Diagram of Solid Wastes in the Drug Industry


MATERIALS
GLASS
PAPER
CARDBOARD
PLASTICS
METALS
FINE CHEMICALS
BACTERIA
FUNGI
LIQUIDS
ANIMAL TISSUES AND ORGANS
ANIMALS
PROCESS
PACKAGE FABRICATION
SOLID FORMULATION (MIXING, GRINDING, TABLETING)
LIQUID FORMULATION
FERMENTATION
EXTRACTION
DISTILLATION
RESEARCH AND TESTING
PACKAGED END PRODUCT
CONSUMER
WASTE'S (PRODUCTION)
PAPER GLASS BOTTLES PLASTIC CONTAINERS CARDBOARD CONTAINERS METAL
DUST & RETURNED & REJECTED DRUGS
CHEMICALS
SPENT LIQUOR
FERMENTATION CAKE
SPENT ANIMAL TISSUE & ORGANS
(NON-PRODUCTION)
EXPERIMENTAL ANIMALS
MANURE
METAL AND GLASS
RADIOACTIVE MATERIALS
WASTE HANDLING
BARRELS BINS MOVABLE CONTAINERS
CRUSHER & SPECIAL HANDLING
LOAD LUGGERS COMPACTORS DUMPSTER BUCKETS
SEWAGE TREATMENT PLANT OF SANITARY SEWER
BARRELS BINS MOVABLE CONTAINERS
LOAD LUGGERS COMPACTORS DUMPSTER BUCKETS
SPECIAL SEALED CONTAINERS
WASTE DISPOSAL
LANDFILL
PRIVATE CONTRACTOR
INCINERATION
SALVAGE
PRIVATE CONTRACTOR
LANDFILL
INCINERATION
COMPOSTING
INCINERATION
SPECIAL LAND DISPOSAL

or publicly owned and operated, are the ultimate disposal areas for all or part of the solid waste generated in the majority of the plants.

Pretreatment of wastes prior to disposal is practiced by many companies. This pretreatment may be limited to selection and sorting of certain solid wastes, wet pulping and/or dry grinding coupled with compaction. Some companies (e.g., the Upjohn Company, Kalamazoo, Michigan) operates on-site incinerators for burning biological tissues (including animal carcasses), waste solvents, waste packaging material and waste laboratory materials. Off-quality products and returned goods are usually ground, wet or dry and buried at land disposal sites.

2. Airborne Wastes

Removal of process and production dusts is a concern of all drug manufacturers. The system employed in removing airborne dusts are similar to those used throughout industry in general. One useful method for removing such substances is the baghouse type dust collector. In fact, some companies exhaust all air from most manufacturing operations through this type of dust collector. The use of this dry filter system is preferred to a scrubber system if problems of water pollution are anticipated.

In addition to problems with airborne dusts, those drug companies involved in the manufacture of antibiotics and other substances produced by fermentation processes have additional problems with airborne contaminants. Most of the fermentations carried out are aerobic, that is, air must be supplied to the fermentation organism. Usually, compressed air is introduced or sparged into the bottom of the fermentation tank which may range in volume from 5,000 to 100,000 gallons. Thus, it is necessary to discharge an equal volume of vent gas from the other end of the tank. The vent gas scrubs several materials from the fermentation as it passes through the reaction, notably carbon dioxide and many complex organic materials which vary with the type of fermentation. Incineration of this vent gas has provided a satisfactory solution to a potential problem. Some companies pipe the vent gas from the fermentor to the boiler house and use it for combustion air in the boiler.

3. Water Wastes

The material most likely involved in water waste problems is the spent beer waste generated by fermentation. This is the fermented broth from which the desired drug fraction has been extracted. The methods of treatment of the liquid fermentation waste are generally biological, trickling filters, or activated sludge. Other techniques employed in the disposal of this waste are:

- Drying by evaporation and sale as animal feed
- Spray irrigation requiring approximately 125 acres/100,000 gallons of spent beer sprayed per day.

An additional type of water waste problem is that associated with chemical wastes and wash water generated during manufacture. In dealing with this type of waste, several techniques are employed. The simplest technique may be a simple pH adjustment to render the waste amenable to the bacteria of the waste treatment plant. However, such wastes and waste water are not always compatible with the biologic systems of the waste treatment plants. Consequently, more rigorous treatment is often required. Added effort includes the precipitation of heavy metals, the elimination of cyanide coupled with the removal of other toxic elements prior to waste treatment. As an alternate route of biologic treatment of chemical wastes, some advances in the acclimation of sewage bacteria to certain chemicals have been made. However, there are still many instances where chemical wastes are too concentrated or too toxic to make this feasible.

4. Radiological Wastes

The preparation of radiopharmaceuticals is a highly specialized area of pharmaceutical manufacture. Where nuclear materials are involved, safety standards are, for the most part, established by the Atomic Energy Commission. Two major sources of radioactive wastes exist...(1) water wastes from process washings, and (2) wastes containing manufacturing residues and off quality products.

Generally, process washings are piped to high capacity storage tanks and are allowed to decay to within safe limits. The storage and decay procedure usually comprises multiple tank arrangements. When one tank is full, additional radioactive waste is directed to a second tank. When the radiation contained in the full tanks has decreased to a safe limit level, as determined by monitoring, the contents are slowly drained into the sewer system.

In disposing of manufacturing residues and off quality products, properly licensed AEC disposal services are normally employed.

5. Animal and Microbiological Wastes

Animal and microbiological wastes are generally subjected to incineration and the ash residue buried at disposal sites. In some instances, the microbiological wastes are sterilized (autoclaving or other suitable means) and are disposed of as land fill without incineration.

6. Solvent Wastes

The bulk of solvents used in production processes are reclaimed by purification techniques. Many companies have installed solvent recovery systems large enought to recover the wide range of solvents used in the production of medicinal chemicals and pharmaceutical formulations

One company is known to recycle 99 percent of the hazardous solvent substances ($>10^6$ gallons/year) used in their facility. Still-bottom residues are given to a contract service for further chemical treatment or incineration. Manufacturing firms using only small volumes of solvent normally employ a contract service to remove them to a disposal site.

7. Wastes Generated by Research Facilities

Quantities of waste materials generated by research operations witnin the drug industry may be small but quite toxic. Increasing amount of work involving radiation emissions has required the installation of special equipment necessary for the prevention of such materials escaping to the air or water effluent. Wastes are collected and treated as production wastes. Similarly, microbiological and animal wastes are incinerated and taken to land fill.

4. ESTIMATES OF WASTE PRODUCTION

Although four site visits were made, useful information regarding quantities and ultimate disposal of potentially hazardous waste materials was obtained from one company. The types and quantity of wastes together with the disposal systems employed are presented in the following summary.

- Solid Wastes, exclusive of solid product material but including cafeteria garbage, construction rubbish, filters and filter aids are drummed and taken to the municipal dump. No estimate of quantity was available.

- Production Wastes including dusts, off quality products, packaging materials, returned goods are handled in one of two ways. A SOMAT process of wet pulping is used for all materials except plastic which is demolished by dry-grinding. Approximately 3,000 cubic yards are compacted monthly and hauled to a publicly owned sanitary land fill by company-owned trucks.

- Process Water Wastes are emptied into the sewage system, approximately 1.6 million gallons per day.

- Radioactive Wastes (process washing) are pumped directly to 10,000 gallon storage tanks for decay. Manufacturing residues and product rejects are given to an AEC disposal service. From 6 - 12 drums (30 to 55 gallon capacity) are disposed of each month.

- Syringes and Needles are destroyed and taken to a land fill. From 20 - 50 pounds per month appear as waste.

- Hazardous Solvents are reclaimed. Approximately 5,000 gallons per month may be given to a contract service for disposal. Additional quantities of solvents (research) are taken by a service company for reclamation. The quantity involved is less than 2,000 gallons per month.

- Mycelia and Fermentation Residue is emptied into the municipal sewer system. However, the company pays for special treatment required to reduce the BOD and COD load at the treatment site.

The estimated annual cost of waste handling by the company is $750,000 which includes municipal cost, contract service fees and maintenance of on-site facilities.

Data describing the waste quantities generated by two of three SIC codes included in the drug industry are presented in Tables A-5-19 and A-5-20. No identification of hazardous waste is made. However, the figures suggest that the drug industry as a whole does not generate excessive quantities of hazardous waste materials. It is certainly one industry that is exceedingly aware of and constantly practicing good housekeeping practices since it is under constant Federal scrutiny. It follows also, that good housekeeping practices assist in controlling the indiscriminate generation or disposal of potentially hazardous wastes. The industry image and Federal requirements demand cleanliness of the operation. The drug industry appears to be essentially a "clean" industry.

Table A-5-19
Drug Industry Wastes (Lbs per Day)

Employees	Garbage	Mixed Production Wastes	Ashes	Street Refuse	Animal Remains	Production Process Wastes	Manures	Undiff. Misc.	Total
SIC 2833									
283		923 (6.5)				13,381 (93.5)			14,304
269		15,411 (25.0)				46,140 (75.0)			61,551
30		100 (64.5)	5 (3.2)			50 (32.3)			155
5						41 (100)			41.4
60		200 (9.1)				2,000 (90.9)			2,200
SIC 2834									
489	150 (7.4)	1,600*(78.5)	10 (0.5)		78 (3.8)		200 (9.8)		2,038
214		5,700 (98.3)					100 (1.7)		5,800
1,800	500 (2.8)	16,000 (90.8)			300 (1.7)	800 (4.5)		25** (0.2)	17,625
133	100 (26.8)	115 (30.8)	4 (1.1)			4 (1.1)		150***(40.2)	373
119		150 (93.8)			5 (3.1	5 (3.1			160
140	20 (3.5)	500 (87.7)				50 (8.8)			570
62	92.3 (66.7)					46.1 (33.3)			138.4
177	100 (2.7)	500 (13.3)	50 (1.3)		10 (0.2)	3,000 (79.8)	100 (2.7)		3,760
36		600 (80.0)				150 (20.0)			750
755	100 (0.3)	36,400 (96.4)		20 (0.1)		1,230 (3.2			37,750
214	10 (1.0	750 (73.5)	100 (9.8)	10 (1.0)		150 (14.7)			1,020
1,400	--4,860 (13.1)--		500 (1.3)		500 (1.3)	17,216 (46.4)	14,000 (37.8)	1**	37,077
736		11,990 (14.9)				49,971 (62.1)			80,468
600	3,000 (12.8)	7,500 (32.1)		600 (2.6)	240 (1.0)	9,600 (41.1)	2,400 (10.3)	7**	23,347
30		180* (100)							180

* Combination of various waste types including process wastes.
** Radioactive wastes.
*** Rejects and returned drugs.

Table A-5-20
Comparison of Total Solid Waste Generated with Employment

Employees	Production Employees	Total Waste Load (Pounds/Day)	Waste Load per Total Employment	Waste Load per Production Employee
475	275	11,160	20.3	40.6
800	370	24,000	30.0	64.9
300	125	52	0.17	0.4
489	192	2,038	4.2	10.6
214	150	5,800	27.1	38.7
283	170	14,300	50.5	84.1
269	216	61,550	222.9	284.9
30	30	155	5.2	5.2
3500	1580	146,690	41.9	92.8
1250		7,105	5.7	
1800	325	17,625	9.8	54.2
6000		95,077	15.9	
5	5	46	9.2	9.2
60	60	2,200	36.7	36.7
298	216	1,710 (1210)**	5.7 (4.1)	7.9 (5.6)
1500	729	32,100	21.4	43.9
133	75	373	2.8	5.0
119	32	160	1.3	5.0
140	77	570	4.1	7.4
62	23	138	2.22	6.0
177	126	3,760	21.2	29.8
36	17	750	20.8	44.1
755	450	37,750	50.0	83.9
214	51	1,020	4.8	20.0
5846	2556	153,969	26.3	60.2
1400	398	37,077	26.5	93.2
736	582	80,468	109.3	138.3
600	150	23,347	38.9	155.6
30	18	180	6.0	10.0

* Mixed production wastes.

** Recent change from disposal to selling of wood pallets gives the lower figures in parentheses.

*** Includes production control employees.

SIC 284—SOAP, DETERGENTS, AND CLEANING PREPARATIONS, PERFUMES, COSMETICS, AND OTHER TOILET PREPARATIONS

1. ECONOMIC STATISTICS

(1) SIC 2841—Soap and Other Detergents, Except Specialty Cleaners

This industry is comprised of establishments primarily engaged in the manufacture of soap, synthetic detergents, inorganic alkaline detergents, or combinations thereof. In addition, establishments which produce glycerin from vegetable and animal fats and oilts are included. Manufacturers producing shampoos or shaving products from soap or synthetic detergents are classified in Industry 2844.

This industry is distributed throughout the United States, with the Middle Atlantic and East North Central Divisions accounting for about 50 percent of the total establishments and those employing 20 or more people (see table below).

Establishments, 1967

Division	Total	20 or More Employees
New England	48	8
Middle Atlantic	166	44
East North Central	166	59
West North Central	47	17
South Atlantic	63	28
East South Central	19	5
West South Central	55	11
West Region	106	35
	668	207

During the 10-year period 1958 to 1967, the number of establishments increased from 608 to 688 or about 10 percent, while the establishments employing 20 or more advanced from 163 to 207 or about 27 percent. Over this 10-year period, the number of employees in the industry increased only 2 percent, with a high of seven percent in 1964. Of the 30,300 employees in the industry, 28 establishments employ about 58 percent of the people (see table below).

Size of Establishment (No. of Employees)	No. of Establishments	Total No. of Employees
1 - 4	287	500
5 - 9	85	600
10 - 19	89	1,300
20 - 49	105	3,500
50 - 99	50	3,500
100 - 249	24	3,600
250 - 499	16	6,000
500 - 999	8	5,500
1000 - 2499	4	5,900
Total	668	30,300

During the period between 1958 and 1967, the industry experienced a growth in shipment value from $1,605.9 million to $2,593.4 million, or about 61 percent. The value added by the manufacturers increased from $857.6 million to $1,403.7 million, or approximately 63 percent. The value of shipments and other receipts from the Soap and Other Detergent industry (in 1967), totaled $2,593.4 million. This total was broken down into three categories: (1) primary products (soaps and other detergents) at $1,990.2 million, (2) secondary products at $405.7, and (3) miscellaneous receipts at $197.5 million.

(2) SIC 2842—Specialty Cleaning, Polishing, and Sanitation Preparation, Except Soap and Detergents

This industry is composed of establishments primarily engaged in the manufacture of furniture, metal and other polishes; waxes and dressings for fabricated leather and other materials; household, institutional and industrial plant disinfectants, deodorants and extermination products; dry cleaning preparations; and other sanitation preparations.

The Polish and Sanitation industry is distributed over the entire United States, with the Middle Atlantic and the East North

Central divisions accounting for about 55 percent of the establishments employing over 50 people, and 46 percent of the total establishments (see table below).

	Establishments, 1967	
Division	Total	20 or More Employees
New England	88	19
Middle Atlantic	247	58
East North Central	211	54
West North Central	99	24
South Atlantic	113	17
East South Central	33	4
West South Central	70	6
West Region	143	21
Total	1,004	203

The 10-year growth period (1958 to 1967) for this industry shows that the total number of establishments decreased from 1,156 to 1,004, or about 13 percent. However, the establishments employing 20 or more people rose from 188 to 203, or approximately 2 percent. The total number of employees in the industry increased from 16,400 to 19,400, or approximately 18 percent. The following table shows the relationship between the use of the establishment and the number of people employed.

Size of Establishment (No. of Employees)	Establishments	Total No. of Employees
1 - 4	527	800
5 - 9	159	1,000
10 - 19	115	1,600
20 - 49	118	3,500
50 - 99	41	2,700
100 - 249	30	4,500
250 - 499	12	5,200
500 - 999	2	Not Given
Totals	1,004	19,300+

During the 10 years 1958 to 1967, the Polish and Sanitation industry experienced a growth in the value of shipments from $585 million to $1,108 million or about 90 percent, and an increase in value added by the manufacturer from $295.6 million to $666.1 million or approximately 122 percent. The value of shipments and other receipts (in 1967) include: primary products at $810.4 million, other products at $199.5 million and miscellaneous receipts at $98.1 million.

(3) SIC 2843—Surface Active Agents, Finishing Agents, Sulfonated Oils and Assistants

This industry is made up of establishments primarily responsible for the production of surface active preparations used as wetting agents, emulsifiers and penetrants. Also included in this category are producers of sulfonated oils and fats, and related products.

The Surface Active Agents industry is concentrated along the eastern coast of the United States where approximately 86 percent of the total establishments operate, and 80 percent of these employ 20 or more people (see table below).

Division	Establishments, 1967	
	Total	20 or More Employees
New England	31	7
Middle Atlantic	64	28
East North Central West North Central	20	9
South Atlantic	31	18
East South Central West South Central	10	4
West Region	8	5
Totals	164	71

The 10-year period 1958 to 1967, shows a growth in total number of establishments, from 142 to 164, of about 15 percent. Those establishments employing 20 or more people grew from 46 to 71 a gain of about 55 percent. The total number of employees in the industry increased from 3,100 to 5,700, or about 83.5 percent. The following table shows the relationship between the size of the establishments and the number of people employed.

Size of Establishment (No. of Employees)	No. of Establishments	Total No. of Employees
1 - 4	34	100
5 - 9	31	200
10 - 19	28	400
20 - 49	47	1,500
50 - 99	13	900
100 - 249	9	2,600
500 - 999	2	Not Given
Totals	164	5,700+

The period between 1958 and 1967 saw the Surface Agent industry's shipment value grow from $126.6 million to $294.2 million or about 130 percent, and the value added by the manufacturer grow from $52.4 million to $129.5 million, for a 150 percent gain. The value of shipments in this industry includes: primary products at $219.1 million, secondary products valued at $59.2 million, and miscellaneous receipts at $15.9 million.

2. DESCRIPTION OF INDUSTRY

Although the Washing industry dates back 2,000 years, no other chemical process industry has experienced such a fundamental reversal of the chemical raw materials and change in the chemical reactions, as was caused by the acceptance of detergents in 1940. Soap was never discovered, but evolved from crude mixtures of alkaline and fatty materials and became an industry in the Thirteenth Century. Chevreul showed that soap formation was a chemical reaction instead of a mechanical mixture of fat and alkali, as it was previously assumed.

Soap is comprised of the sodium or potassium salts from various fatty acids such as oceic, stearic, palmitic, lauric, and myristic acids.

(1) Soaps

Soap, as manufactured by the old kettle process, is now used only in smaller factories or for special or limited production. This process was replaced by a continuous alkaline saponification process, which can produce as much soap in two hours as the older batch method could produce in two to five days (at 300 tons/day). The present method of soap manufacture is the continuous splitting or hydrolysis process, in which fatty acids are neutralized into soap after the separation of glycerin.

Raw materials for the manufacture of soap include:

- Tallow — This principal fatty material (in soapmaking) represents 75 percent of the fats and oils consumed.
- Grease — This second most important material represents 20 percent of the consumed materials obtained from hogs and small domestic animals.

- Coconut Oil — This produces a soap that is firm and lathers well, also contains large proportions of desirable glycerides of lauric and myristic acids.
- Chemicals — These include caustic soda, salt, soda ash, caustic potash, sodium silicate, sodium bicarbonate, and trisodium phosphate. These are used primarily in the role of soap builders.
- Free Fatty Acids — These are the basic materials for manufacturing wax.

(2) Detergents

Detergents are manufactured by using the continuous saponification process developed by Sharples and Lever Brothers in 1945. The process (sulfonacation-sulfation) starts with alkylbenzene being introduced into the sulfonator with the proper amount of oleum. The dominant bath principle is used to control heat of sulfonation conversion and to maintain the proper temperature. Fatty tallow, alcohol, and additional oleum are added to the sulfonated mixture. All of this is pumped through a sulfater, operating on the dominant bath principle to maintain temperature and producing a mixture of surfactants. This is followed by a neutralization process where the sulfonated-sulfated product is neutralized with a sodium hydroxide solution. The temperature is controlled to maintain fluidity of the surfactant slurry, which is conducted to storage.

The surfactant slurry is introduced into the crutcher, together with the sodium tripolyphosphate and most of the other additives. Considerable water is removed and the paste is thickened by a tripolyphosphate hydration reaction. The resulting mixture is pumped to an upper story where it is sprayed, under high pressure, into a spray tower, counter to hot air from the furnace. Here the granules are formed. These are transferred again to an upper story by air lift where they become cool and stabile. Finally, they are separated in a cyclone; screened, perfumed, and packed.

The raw materials for the manufacture of detergents include:

- Surfactants — These surface active agents include soaps, detergents, emulsifiers, wetting agents and penetrants (SIC 2843), and compounds that affect surface tension when dissolved in water. The surfactants of both soap and synthetic detergents act to perform the cleaning and sudsing of the washing action by reducing surface tension. The cleaning action consists of three main steps: (1) wetting the dirt and surface with soap or detergent, (2) removing dirt from the surface, and (3) maintaining dirt in the solution until removal through detergent action and mechanical agitation. Surfactants are classified as:
    - Hydrophobic
    - Hydrophilic
    - Anionic
    - Cationic

- Nonionic
- Zwitterionics
- Semipolar.

- Suds Regulators — This is an ingredient usually used with a surfactant to stabilize or suppress the generation of suds. It usually consists of hydrophobic materials. Examples of suds suppressors are long-chain fatty acids, silicones, and hydrophobic nonionic surfactants. Examples of stabilizer surfactant systems are lauric ethanolamide-alkyl-benzene sulfonate and lauryl alcohol-alkyl sulfate.

- Builders — These elements are used to boost detergent power and consist almost exclusively of complex phosphates such as sodium tripolyphosphate. The rapid rise in the acceptance of detergents stemmed from the building action of these polyphosphates.

- Additives — These make up about three percent of the detergents. These include corrosion and tarnish inhibiters, brighteners, bluings, antimicrobiologicals, bleaches, perfumes, and colorings.

(3) Glycerin

Glycerin is a clear liquid having a sweet taste but no odor. It was first prepared by Scheele in 1779; in 1846 Soberero produced the explosive nitroglycerin; and, in 1868, Nobel made it as safe to handle as an explosive. These discoveries increased the demand for glycerin. Glycerin is produced from organic raw materials and may also be derived synthetically from petrochemical raw materials. In 1962, a total of 549 million pounds was produced; 118 million pounds (47 percent) was produced synthetically.

Glycerin is produced by a number of different methods: (1) saponification of glycerides (oils and fats) in soap production, (2) hydrolysis, or splitting of fats and oils in the production of fatty acids, and (3) chlorination and hydrolysis of propylene and other reactions from petrochemical hydrocarbons. The recovery of glycerin from the soap plant involves energy, primarily in the form of heat consumption for evaporation and distillation. The first step in the production of glycerin from organic raw materials includes:

- Evaporation (multiple effect) for concentration
- Purification with settling
- Steam vacuum distillation
- Partial condensation
- Decoloration (bleaching)
- Filtration or ion-exchange purification.

Most natural glycerin is produced from natural fats and oils by the hydrolysis method. The process is carried out, with a catalyst, in a large continuous reactor at elevated temperature and pressure. Water flowing countercurrent to fatty acids extracts glyceral from the fatty phase. The resulting sweet water, containing about 17 percent glycerol, is fed into a triple-effect evaporator. Here the glyceral concentration is increased to 75 or 80 percent (hydrolyzer crude). This concentration, when settled, contains 78 percent glyceral, .2 percent fatty acids, and 22 percent water. After settling, it is distilled. A small amount of caustic is added to saponify fatty impurities. Final purification of glycerin is accomplished by carbon bleaching, followed by filtration or by ion-exchange.

3. WASTE CHARACTERISTICS

(1) Biodegradability of Surfactants

Since the surfactants are disposed of into the sewage treatment plants or surface streams, the effect of microbial action on the surfactant is important. Some of these, such as tetrapropylene-derived alkyl-benzene sulfonate, degrade slowly with a persistent residue. Others are more readily decomposable by micro-organisms and leave practically no persistent residue. The ease with which surfactants are dissassociated is termed biodegradability. Tests measuring the die-away rate of surfactants in river waters, or which stimulate the biological process employed in sewage treatment plants, are being used for biodegradability measurements. Work is continuing in this area.

(2) Pollution

The eutrophication of lakes and streams due to soaps, detergents, and allied products results from too many nutrients or "fertilizers" being deposited in our waters. These nutrients, which feed algal growth, include carbon, nitrogen, iron, and (depending on the water) some 10 or 15 other chemical elements. They also include phosphates which come from household laundry detergents. The detergent industry has undertaken a massive voluntary program to reduce the phosphate content in its laundry products, thereby reducing this type of pollution. The magnitude of this effort is indicated by the fact that, to this date (October 1970), the industry has reduced the consumption of phosphates by 100 million pounds per year. By early 1972, this figure is estimated to reach 641.2 million pounds per year.

(Note:) Information for this section was obtained from References 8 and 9.)

SIC 285 - PAINTS, VARNISHES, LACQUERS, ENAMELS, AND ALLIED PRODUCTS

1. ECONOMIC STATISTICS

This industry is made up of establishments primarily engaged in the manufacture of paints (paste or ready-mixed), varnishes, lacquers, enamels, shellac, putties and caulking compounds; wood fillers and sealers, paint and varnish removers, paint brush cleaners and allied paint products.

The Paint and Allied Products industry is distributed fairly evenly throughout the North East, North Central, South and Western regions, with the North East and North Central region containing about 62 percent of the industry (see table below).

	Establishments (1967)	
Division	Total	20 or More Employees
New England	98	30
Middle Atlantic	445	165
East North Central	402	183
West North Central	107	49
South Atlantic	175	70
East South Central	54	28
West South Central	112	47
Mountain	26	8
Pacific	282	100
	1,701	680

During the 10-year period from 1958 to 1967, the Paint and Allied Products industry decreased in total number of establishments from 1,709 to 1,701 or about 0.5 of 1 percent, while the number of establishments employing more than 20 people increased from 600 to 680 or about 13 percent. The number of employees during the same period increased from 58,800 to 66,100, or approximately 12.5 percent. The following table shows the relationship between establishments and people employed.

Size of Establishment (No. of Employees)	No. of Establishments	Total No. of Employees
1-4	468	900
5-9	242	1,700
10-19	311	4,300
20-49	350	11,100
50-99	171	12,000
100-249	113	17,100
250-499	36	11,900
500-999	8	7,100
1000-2499	2	(NA)
	1,701	66,100+

During the 10-year period from 1958 to 1967, the Paint and Allied Products industry experienced a growth invalue of shipment from $1,878.7 million to $2,911.4 million or about 55.5 percent, and an increase in value added by the manufacturer from $806.9 million to $1,318.5 million or approximately 64 percent. The value of shipments and other receipts for this industry (in 1967) totaled $2,911.4 million broken down into primary products of $2,598.5 million, secondary products of $133.0 million, and miscellaneous receipts of $179.8 million.

2. DESCRIPTION OF INDUSTRY

(1) Paints

A paint consists essentially of a pigment, suspended in a suitable liquid, called a vehicle. This may be a drying oil, varnish, solution, or a suspension of natural or synthetic resins in an organic water solvent. When spread in a thin film, the volatile components evaporate, leaving a mixture of pigment and binder in the form of a continuous solid coating that is both decorative and protective.

Oil-based paints dry by oxidation and polymerization of the vehicle; there are hastened by driers and catalysts consisting of oleates, resinates, or oxide of cobalt, lead, magnesium, iron, calcium, zinc or zinconium. Solvents or mineral spirits are used to decrease viscosity as an aid in application.

Water-based paints were of small importance prior to World War II, but now hold 20 percent of the do-it-yourself market. This represents a fifteen-fold increase in the past 10 years. In the next 10 years, water-based paints are expected to become of major importance for exterior finishes, not only for houses but for automobiles as well.

There are several methods for preparing paints, but all require a homogeneous dispersion of the pigment in the vehicle. This is usually done by grinding methods, such as:

- Roller mill—A series of water-cooled, hardened steel rollers, turned at different speeds and in opposite directions
- Pebble mill—Pigment and vehicle are placed in a porcelain-lined water-cooled pebble mill, which is about half full of pebbles the size of golf balls.
- Moorehouse mill—This is a commercial adaptation of a laboratory colloid mill. Small in size, it is a high speed continuous mill used for house paints, flats and water emulsion finishes.
- Stone mill—Mixing by grinding between stones, as has been done for ages, is still used where a fine grind is desired and capacity is not important.
- Sand process—This most recent development for pigment dispersion, consists basically of a bucket of sand (controlled particle size) rapidly agitated by hardened steel discs. A pigment-vehicle mix of low viscosity is passed through the sand.

(2) Varnishes and Enamels

A varnish differs from an enamel in that it contains no pigment, and produces a clear transparent coating. Most are oleoresinous materials made by cooking drying oils and resins, and then adding drying oils and thinners. Drying oil is generally tung oil, while the resin is estergum or a special synthetic resin. However, other oils may be used. The ratio of resin to oil varies with the different types of varnish used for different purposes (see table below).

Oil	Gallons Used per 100 lb. Resin	Purpose
Short	12-15	Furniture (rubbing)
Moderately Short	15-25	Household enamels
Medium Length	25-35	Spar and floor varnish
Long	35-50	Durable exterior finishes

In making a typical varnish, the gum resin and oil are heated in a kettle over an oil burner. The temperature rises rapidly to 500-600° and is maintained until the mixture becomes homogeneous. Driers are added during the cooking process. The kettle is pulled from the fire, and its content is cooled and thinned. Dirt is removed after cooling, and a liquid drier is added after thinning. The final product, varnish, is then pumped into storage tanks to await production control tests. (Baking japans are varnishes made with asphaltum instead of resin.)

Varnishes and enamels are classified as follows:

- Oleoresinous varnishes and enamels
- Alkyd varnishes and enamels
- Cellulose clear lacquer and lacquer enamel
- Resin lacquers and enamels.

(3) Lacquers

These protective coatings dry by evaporation of volatile components. The film-forming constituent is usually a cellulose ester (nitrate, acetate or acetate-butyrate), combined with a resin. Plasticizers are incorporated to add flexibility to the film. Acrylics and other thermoplastic polymers are now being employed in lacquer systems. In addition to nitrated cotton, a nitro-cellulose lacquer contains: (1) a solvent mixture which includes a ketone, an alcohol, a volatile ester and an ether-alcohol; (2) a resin such as alkyd, a phenolic or an ester gum; (3) a plasticizer for film flexibility, (4) volatile diluents, and, (5) a dye or pigment.

Lacquer is made by first dissolving the selected resin in the diluent and then adding this to the cotton-solvent solution. Finally, the pigment is added, as a suspension, in a nitro-cellulose solution or in the plasticizer. A tank with an agitator is used for these operations.

The main uses for lacquers are automobile finishes, woodwork and furniture, and artificial leather. Artificial leather is made by coating cotton fabric with a pyroxylin solution and then embossing it to simulate the grain of leather. The following table shows amounts of the various components found in paints and allied products (Reference 9).

Materials	Billions of Pounds
Pigments and colors	2.1
Solvents and thinners	2.0
Resins	0.8
Drying oils	0.7
Plasticizers, polyols, and miscellaneous	0.4

(4) Pigments

Although, the Pigment industry is separate from that of the Paint and Allied Products industry, almost half of the Pigment industries' product is consumed in paints and allied products. Approximately 35 percent of the total Pigment industry materials (in 1958) were used in the manufacture of paints, varnishes, enamels and lacquers. Some materials and processes used in the production of pigments are:

- Titanium Dioxide—Produced by mixing sulfuric acid with concentrated ore. After digestion and solution, the liquor is filtered. The concentrate is boiled in sulfuric acid where titanium dioxide is precipitated. The precipitate is washed, dried, calcined and ground. This pigment, with controlled caulking, is used exclusively for house paint.

- White Lead—Prepared by several processes: (1) the Dutch process requiring three months, (2) the Carter process requiring two weeks, and (3) the French process requiring two days. The white lead dust is poisionous and constitutes a health hazard; hence, it is usually wet ground. White lead is the sole pigment in oil-based paint which provides an adherent, tough, elastic and durable exterior paint.

- Zinc Oxide—Prepared by the French process. Zinc metal is heated, in stoneware retorts, vaporized and burned in a combustion chamber. The white dust from this process is collected and prepared as a pigment. There is a direct process where the oxide is prepared directly from the ore. Zinc oxide is also used, primarily for exterior house paint.

- Litharge (Lead Oxide)—Produced by heating metallic lead in a reverbratory furnace, where it is kept just above the melting point with large volumes of air flowing over it. The oxide formed is drawn off the surface, cooled, ground and levigated.

- Red Lead—Produced as a byproduct in the manufacture of sodium nitrate, and by calcining litharge in a muffel furnace. Production of red lead now surpasses that of white lead.

- Iron Oxide—Produced by roasting ferrous sulfate obtained from the vats used for pickling steel. The shade of this pigment is varied by altering the firing time, temperature and atmosphere. It represents a cheap source of pigment widely used as red barn paint and metal primer.

- Carbon Black—Consists of several different types:

    - Thermal black—Pigment produced by thermal decomposition of natural gas.

- Channel black—Deposit collected when many small regulated flames impinge on a relatively cool surface.

- Furnace black—Partial combustion of fuel gas in a furnace; recovery is by cyclone or precipitator.

- Lamp black—Residue as free soot or smoke collected in chambers burning oils of hydrocarbon gases.

- Prussian Blue—Produced by reacting sodium ferrocyanide, ferrous sulfate and ammonium sulfate. The precipitate is then oxidized with sodium chlorate or sodium dichromate.

- Phthalocyanine Blue—Produced as greens and blues with a high tinting strength. They are expensive, but very effective tinters, and are used in both oil and water-base paints.

- Ultramarine Blue—Produced by heating a mixture of soda ash, clay and sulfur with charcoal and pitch. Its use is chiefly in exterior paints.

- Chrome Yellows—Produced by precipitating soluble salts from solution containing sodium or potassium dichromate. It has high tinting strength. The color shades are adjusted by varying the pH of the precipitating solution.

- Chrome Greens—Manufactured by co-precipitating Prussian blue and chrome yellow. The color depends upon the mixture ratio of the two pigments used.

- Natural Pigments—Consist of umber, ochre and sienna.

- Metallic Pigments—Consist of metallic powders mixed with a suitable vehicle.

- Luminescent Pigments—Consist of organic dyes of the rhodamine, auramine and thioflaving types. The paints are used in advertising displays and on aircraft because of their daylight brillance.

3. WASTE CHARACTERISTICS

(1) Solvent Emissions

The emission of organic vapors into the atmosphere is objectionable because of the photochemical reactions in which they take part. Certain organic vapors react with oxygen and nitric oxide to produce smog components which, in turn, produce eye irritation, plant damage, visibility reduction, etc. Hydrocarbons are important because they make up about 85 percent of the organics in the atmosphere. In general, olefins react rapidly, while aromatics react more slowly. Benzene is unreactive, while xylene and most substitute-aromatics (common in solvents) react as rapidly as olefins. Table A-5-19 shows a breakdown of constituents, with regard to the volatility of purchased surface coatings.

The concentration of organic solid vapor emissions released by most surface coating operations, ranges from 100 to 200 parts per million (one pound of solvent vapor per 40,000 cubic feet of air). There is a hazard of the solvent concentration building up to explosive proportions, although it is common practice for industry to limit the concentration to one-fourth of the lower explosive limit (approximately 2,500 ppm for common solvents). The procedure for the recovery and removal usually involves one of these procedures: (1) condensation, (2) adsorption, (3) vapor incineration, and (4) adsorption.

Table A-5-19
Composition of Commercial Surface Coatings

Type of Surface Coating	Composition By Percent					
	Non-Volatile	Hydrocarbons		Alcohols	Ketones	Esters and Ethers
		Aliphatic	Aromatic			
Paint	44	56	-	-	-	-
Varnish	50	45	5	-	-	-
Enamel	58	10	30	2	-	-
Lacquer	23	7	30	9	22	9
Metal Primer	34	33	33	-	-	-
Glaze	80	-	20	-	-	-
Resin*	50	-	-	-	-	-
Sealer	50	40	-	-	-	10
Shellac	50	-	-	50	-	-
Stain	20	-	80	-	-	-
Zinc Chromate	60	-	40	-	-	-

* 50 percent unspecified solvent type.

(2) Surface Coating Mists

During spray painting operations, the paint becomes mixed with the atmosphere. Breathing these vapors, many of which are toxic, constitutes a serious health hazard to anyone in the surrounding area. In addition, continual use of paint products, where contact with the products is frequent, leads to certain medical problems. These may ensue as a result of the toxic effects of some of the coating constituents, and by inhaling the paint vapors.

(Note: Information for this section was obtained from References 8 and 9.)

SIC 287 - AGRICULTURAL CHEMICALS

1. ECONOMIC STATISTICS

The agricultural chemicals industry is composed of three subcategories:

SIC 2871 - Fertilizers

SIC 2872 - Fertilizers, Mixing Only

SIC 2879 - Agricultural Pesticides, and Other Agricultural Chemicals, Not Elsewhere Classified

SIC 2871 comprises establishments primarily engaged in manufacturing mixed fertilizers (mixtures containing nitrogen, phosphoric acid (P_2O_5) or potash) from one or more fertilizer materials produced in the same establishment. When sulfuric, phosphoric, or nitric acid plants report other activities separately they are classified as part of SIC 2810 - Industrial Inorganic Chemicals. When separate data is not provided, captive plants are classified in this industry.

SIC 2879 comprises establishments primarily engaged in the formulation of ready to use agricultural pest control chemicals. Establishments primarily engaged in manufacturing basic or technical agricultural pest control chemicals are in SIC 2871. These chemicals, including insecticides, fungicides, and herbicides such as lead and calcium arsenates, copper sulfate, DDT, BHC, 24D, carbonates, etc., are classified as part of 281 industrial chemicals.

SIC 2872 is engaged in mixing fertilizers manufactured in other industries.

The geographical distribution and relative size of the various establishments is shown below:

	SIC 2871		SIC 2872		SIC 2879	
Division	Establishments With 20 or More Employees	Value Added ($ Millions)	No. of Establishments	Value Added ($ Millions)	No. of Establishments	Value Added ($ Millions)
New England	-	-	5	(D)		
Mid-Atlantic	6	(D)	22	(D)	21	53.3
East North Central	39	41.7	44	66.9	9	37.1
West North Central	12	17.2	18	16.5	11	41.1
South Atlantic	64	179.0*	86	57.6	25	26.5
East South Central	29	67.4	15	10.4	10	131.1
West South Central	19	53.9	12	11.9	12	24.4
Mountain	8	9.3	2	4.2	6	33.2
Pacific	5	18.7	6	9.9	18	28.6
Total	184	434.1	210	195.3	115	376.3

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*Florida - $167.2 million

The interrelationships between these industries and others in the chemical industry are shown below:

Total Shipments ($Millions)

	All Industries	SIC 2871	SIC 2872	SIC 2879	Other Industries
Totals	x	1196.9	731.1	817.0	x
Fertilizers	982.8	933.6	12.4	2	20-50
Fertilizers Mixing Only	588.2	2	570.1	4.8	10-20
Agric. Chemicals	834.3	2-5	5-10	598.5	223.9
2815	x	-	-	2	x
2818	x	2-5	.6	14.9	x
2819	x	145.5	-	4.3	
2851	x	-	-	10.2	x
Misc. Receipts	x	108.8	137.5	130.1	x

The basic materials consumed (1967) in making fertilizers are illustrated by the following table:

2871 Fertilizers	1000 Short Tons	Delivered Cost ($)
Nitrogenous Materials	1,560	87.4
Phosphatic Materials	430	51.0
Potassic Materials	2,535	69.8
Sulfuric Acid	3,375	50.7
Phosphate Rock	12,485	116.9
Phosphoric Acid	272	45.8
Sulfur	2,965	108.1
Containers		14.0
All other materials & components		123.0
Totals	23,622	667.8

2872 Fertilizers	1000 Short Tons	Delivered Cost ($)
Nitrogenous Materials	1,122	84.7
Phosphatic Materials	770	89.3
Potassic Materials	1,482	56.5
Inert Fillers	808	8.7
Sulfuric Acid	175	4.0
Phosphate Rock	80	-
Phosphoric Acid	145	15.8
Bags	-	13.0
All other materials	-	146.4
Totals	4,582	417.4

The sale of pesticidal chemicals in 1967 was:

Fungicides	178,000,000 lbs
Herbicides	348,300,000 lbs
Insecticides, fumigants & Rodenticides	504,300,000 lbs
Grand Total	1,030,600,000 lbs

2. PRODUCTION AND WASTE CHARACTERISTICS

The following discussion is divided into the production processes associated with chemical fertilizers and those associated with the prodcution of pesticides.

(1) Chemical Fertilizers

The materials used by the fertilizer industry are found in natural deposits, salvaged from industrial and sewage wastes, or manufactured synthetically. Each of the primary nutrients, phosphorus, nitrogen, and potassium, is derived from nature sources by processes unique to each chemical. The following paragraphs outline the major extraction processes.

1. Phosphates (Phosphorous).

Processing phosphatic materials is the oldest manufacture and actually forms the basis of the industry. Phosphate rock is the principal source of phosphorus. Phosphatic minerals occur chiefly as amorphous or crystalline apatite and its variants such as calcium hydroxylapatite. Other sources of phosphorus are basic slag, bones, and guanos.

Sulfuric acid, used to convert phosphate rock to more suitable forms, is manufactured by the contact process. Gaseous SO_2 and SO_3 emissions are the principal pollution sources. There are no inherent water pollutants, but heat removal using water is essential and, thus, some cooling treatment is necessary.

Most of the phosphoric acid used is manufactured by the wet process method, using sulfuric acid, although nitric and hydrochloric acids may also be used. The sulfate component of the sulfuric acid combines with the calcium according to the following reaction:

Phos. Rock + Sulfuric Acid + Water → Gypsum and M-Phosphoric Acid

The insoluble gypsum is then separated. As a result of the process, water streams may become contaminated with fluorine which may be liberated in the reaction.

If nitric acid acidulation is used, the reaction is:

Phos. Rock + Nitric Acid → Calcium Nitrate + Phos. Acid

By ammoniation with anhydrous ammonia the calcium nitrate is then converted to other calcium compounds and soluble ammonium nitrate (NH_4NO_3) which are then processed directly into solid fertilizer. Ammonia (NH_3), HF, and SIF_4 are by-products released to the atmosphere.

If hydrochloric acid acidulation is used the following products result

Phos. Rock + Hydrochloric Acid → Calcium Chloride + Phosphoric Acid

The updgrading of wet process phosphoric acid to a more commercially acceptable state involves either concentration or the partial removal of impurities. Fluorine is the principal impurity evolved which contaminates the water. Settling and/or centrifugation physically separates precipitated impurities. Due to the high P_2O_5 content of the impurities, they may be assimilated in the production of solid fertilizers.

2. Ammonia (Nitrogen)

Ammonia forms the basis for the nitrogen fertilizer industry. Nearly all ammonia is synthetically produced. Nitrogen is extracted from the atmosphere and catalytically reacted with hydrogen. The hydrogen may come from solid, and heavy liquid feeds (coke, wood, fuel oils) or light liquid feeds and gases such as natural gas, coke oven gas, refinery tail gases or electrolytic hydrogen. Over 96 percent of synthetic ammonia produced is from natural gas. Small traces of sulfur compounds are removed from the natural gas and vented to the atmosphere. Wastewater may contain phosphates, sulfates, and sulfites. Carbon dioxide, carbon monoxide, and water vapor are also produced as side products.

The production of ammonium nitrate involves several steps. Final nitric acid (HNO_3) is produced by the catalytic oxidation of ammonia with air. Then ammonium nitrate (NH_4NO_3) is produced by reacting ammonia and nitric acid to form ammonium nitrate, a basic fertilizer.

The major source of pollution in all ammonium nitrate plants is from floor spillings and ammonium nitrate dust.

Urea (NH_2CONH_2) is produced by combining ammonia and carbon dioxide. Urea plants are located adjacent to ammonia plants, which supply both the ammonia and the carbon dioxide requirements of the urea plant. Water vapor and air, containing traces of urea are vented to the atmosphere. Spills are recovered.

3. Potash (Potassium)

Potash constitutes one of the major nutrients essential for plant growth. The element is widely dispersed in nature, occurring in highly soluble salts such as potassium-bearing silicates, and in marine and land plants.

Practically all commercial potash is recovered from potash-bearing brines or from underground deposits of soluble minerals. Extraction by solution and recrystalization is commonly used. Separation of potash from its ore by mineral flotation is also widely practiced.

Potassium chloride, or muriate of potash, is the major source of potash in fertilizers. Potassium sulfate, also a major component of fertilizers, is made by reacting potassium chloride with sulfuric acid to form potassium sulfate and hydrochloric acid. Other potassium compounds include potassium nitrate and potassium carbonate.

Potassium nitrate (KNO_3) is produced by reacting potassium chloride and nitric acid to form potassium nitrate, nitric acid, and hydrochloric acid. Potassium carbonate (K_2CO_3) is generally made by the carbonation of potassium hydroxide.

Generally speaking, with the exception of specialized crops, one potash fertilizer is as effective as any other as a source of potash for the plant.

4. Storage Problems

The storage of some fertilizer intermediates and final products may create pollution problems, especially with normal superphosphate and triple superphosphate. The curing of these fertilizers produces fluorine. Fluorine is also released during processing. At that time scrubbers are used to remove the fluorine.

The physical process of transporting fertilizer materials—both liquid and solid types—can contribute to water pollution. Cleaning of a railroad car or tank before loading and accidental spills create the problems. Shipping losses range between 0.25-1.00 percent of the total material shipped.

(2) Pesticides

Pesticides include a wide range of chemicals used to control or destroy insects, weeds, etc.

There are approximately 45,000 pesticide formulations using some 900 chemicals. Although each is meant to be toxic to only certain forms of life, they may enter the environment as a contaminant and may affect other forms of life directly or indirectly.

Pesticide manufacturers produce many pesticide wastes. Some are neutralized or degraded at the production site. Minor amounts are carried by rain and washwater onto the plant site. The major amounts are found in cleanup wastes. One source generally overlooked is the pesticide residues in the laundry waste water from the washing of protective clothing worn during manufacturing. Unless the waste treatment is a hundred percent effective, the effluent may contain pesticide residues as high as 1 part per billion. The sludge or settleable matter remaining after treatment contains most of the pesticides found in the influent. The disposal of these solids presents a major pollution problem. The salvaging of drums which contain emulsifiable solutions of pesticides may be another source of contamination if the washwater from drum salvaging is allowed to enter into a watercourse.

Formulating plants receive pesticide concentrates from manufacturers. After dilution, the final pesticide formulation is repackaged, loaded, and shipped to wholesalers. Pesticide spillage is usually washed or brushed into drains. Also, dust from formulation methods collects at the plant site.

Wholesale pesticide merchandizing is susceptible to pesticide spills. Empty drums can continue to retain several ounces of pesticide, and, as discussed previously, washwater from drum salvaging can present a disposal problem.

Air pollution hazards are always present in the manufacture, formulation, and packaging of pesticides. Pesticides are usually made in closed systems of a continuous-process with usually a slightly negative pressure to avoid leakage. Little data exists on the emission rates of pesticides from production plants.

Drum reconditioning operations may result in occasional contributions of pesticide residues and wastes to sewage systems and streams. Usually, 55-gallon drums are spot cleaned, burned out, or flushed out during the cleaning process. Frequently, informal indisposal of a variety of containers is in open ditches or other "out-back" locations contributes to water contamination by pesticides.

3. DISPOSAL PRACTICES

(1) Fertilizer Manufacturing Wastes

The basic pollutants which arise from manufacturing operations in the fertilizer industry are shown in Table A-5-9, following this page.

Sulfuric acid mist is removed by precipitators and must eliminators. Many of the plants are of the single absorption type which emit from 1500 to 2500 ppm of sulfur dioxides from their stacks. A small number of more modern plants are using the double conversion process which reduces emissions to as low as 500 ppm.

Nitrous oxides are removed by catalytic reducers in many plants but are not fully successful in eliminating all emission. Advanced units are capable of virtually eliminating all oxides but adequate industrial performance data has not been obtained.

Ammonia gas is captured by acidic scrubbers. Newer plants have reduced nitrogen oxide losses to less than 0.5 pound of nitrogen per ton of ammonia produced, less than 5 percent of the loss typical of plants built over 25 years ago.
Ammonia losses from urea plants are 2 to 3 pounds per ton of product. Catalytic reduction and wet scrubbing reduce losses. Ammonia losses from pressurized containers, when in shipment, may present a serious hazard.

Table A-5-9
Summary of Fertilizer Production Wastes

Products	Summary of Fertilizer Production Wastes Waste Description	 Quantities	Waste Process
Phosphate Fertilizers Sulfuric Acid	Sulfur Dioxide Gas	Minor	Scrubbers
Phosphate Rock Grinding	Dry Process - Dust	Substantial	Bag Collector
Phosphoric Acid (41%)	Flourine Gas- Gypsum (3 CA· SO_4· 2 H_2O)	Limited 5 Tons Gypsum/Ton H_3PO_4	Scrubbers Sedimentation only or precipitation with lime.
Upgrading Phos. Acid to 55-75%	Fluorine - Other w/Product	Minor	Scrubbers
Super Phosphate H_2SO_4 Phos. Rock	SiF_4	Substantial	Scrubbers
Triple Super Phosphate Phos. Rock H_3PO_4 Acid	SiF_4	Substantial	Scrubbers
Mono Ammonium Phosphate ($H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$ + Heat)	Minor $\left\{\begin{array}{l}N^*\\P_2O_5\\F\end{array}\right.$ (Less then) (2#/Ton)	—	Scrubbers Sedimentation ponds
Di Ammonium Phosphate ($NH_4H_2PO_4 + NH_3 \rightarrow (NH_4)_2HPO_4$)	Recycle excess NH_3	—	—
N-P-K Fertilizers (Mix H_3PO_4 NH_4NO_3 or $(NH_4)_2SO_4$ with KCl slurry which is spray dried)	Cl_2 NH_3 Gases	Limited	Scrubbers
Nitrogen Fertilizers Natural Gases	SO_2 CO_2 CO (See Table _)	Limited	Scrubbers
Ammonia	Oil Catalysts NH_3 - Caustics	Limited	Skimming Sedimentation
Nitric Acid	Little or none	–	–
Ammonium Nitrate ($NH_3 + HNO_3 \rightarrow NH_4NO_3$)	Little or none	–	–
Urea ($2NH_3 + CO_2 \rightarrow NH_2CONH_2 + H_2O$)	Little or none	–	–

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* No commercially proven process for removing N from water solution.

Fluorine compound emissions as gases or particulates and in scrubbing water is the most difficult hazard to control. Exit gases from mono and diammonium phosphate and granulation plants are reduced by scrubbing. Fluorine compounds produced from mixing single and super phosphates are also scrubbed from emissions. Curing sheds which by and large do not have ventilation control are major sources of fluorine loss. All scrubber wastes must be treated with lime to precipitate the fluorine compounds in settling ponds.

Particulate emissions are particularly heavy from phosphate rock drying and grinding operations and from dry processing and sizing plants. Bag collectors and electrostatic precipitators currently in use do not meet existing removal standards.

The major pollutant from phosphate extraction is gypsum. Approximately 5 tons are accumulated for each ton of super phosphate produced. Over 20 million tons are generated annually, most of it in Florida. These slimes are returned to the areas from which dredged. In the extraction process, the addition of water increases the bulk of the residuals beyond that of the original material. Means to effectively dewater such slimes are needed to restore the land which has been torn up from cut nd fill operations. Rapid dewatering of these sledges would create compact land fill coupled with lakes, an ideal combination in Florida.

Raw water is constantly treated to remove sediments and to cool for reuse in manufacturing operations. The type treatment required by the water wastes associated with the production of phosphoric acid and phosphorous is shown in Tables A-5-20 and A-5-21.

The effluents from mixed fertilizer operations are largely made up of fertilizer components which have entered waste streams. Coagulation and sedimentation are used to remove wastes. Contamination of water by nitrogen from such operations occurs. To date there is no commercially proven process of removing nitrogen from water streams.

Spills are reclaimed as completely as possible. Wet scrubbers remove pollutants (such as fluorine as SiF_4) and the scrubber effluent is then treated. Drainage collected is either treated or pumped to a confined area where overall plant pollutants are contained. Dust collection systems prevent minor product wastes from accumulating.

Generally speaking, solid fertilizer plant effluents are combined with complex phosphoric acid plant effluents and the

Table A-5-20
Base Levels of Treatment and Best Available Treatment for Wastes from Manufacture of Phosphoric Acid

Process	Wastes	SRWL (lbs/ton H_3PO_4)	Base Level of Treatment	Resultant Effluent	Best Available Treatment	Resultant Effluent
Acidulation	$CaSO_4$ (as S)	1580	settling pond, process water recycle (except during periods of high rain)	0-2000 ppm $CaSO_4$	same as base level treatment	0-2000 ppm $CaSO_4$
"	CaF_2 as $F^{=}$	68	settling pond, process water recycle, double lime treatment	5-8 ppm	settling pond double lime treatment (>24 hour retention)	<5 ppm
"	Phosphates	45	settling pond, lime treatment to pH 10	0.5-5 ppm $PO_4^{\equiv}$	same as BLT with >24 hour retention	<0.5 ppm $PO_4^{\equiv}$
"	Silicates	170	settling pond	<0.5 ppm	same as BLT	<0.5 ppm
Dry	H_3PO_4	1.0	use of washdown water for H_3PO_4 manufacture or no treatment	0-1.0	use of washdown H_2O for H_3PO_4 mfg.	0
"	As_2S_3	0.3	special burial or ponding with pH control	0	special burial	0

Table A-5-21
Base Levels of Treatment and Best Available Treatments for Wastes from Phosphorous Production

Specific Waste	SRWL (lbs/ton P_4)	Base Level of Treatment	Effluent	Best Available Treatment	Effluent
Phosphorous	12	variable, disposal by burial in various ways	0	burial	0
Soluble Phosphates	10.5	lime treatment settling pond	7.5 mg/l	lime treatment, settling pond and recycle of process water	0
Fluorides	7.6	lime treatment and settling pond	1.0 mg/l	lime treatment, settling pond and recycle of process H_2O	0
Solid Phosphates	115	dry collection and recycle	0	dry collection and reuse	0

composite is then treated, but it must be remembered that any chloride ion presence requires separate treatment due to the possibility of heavy corrosion. Also, chloride ion will solubilize some water insoluble P_2O_5 compounds which are present in plant effluents. Overall, pond areas of sufficient size are used to permit settling of particulates. Aeration with activated sludge is a method being tested.

(2) Pesticide Manufacturing Wastes

Control of wastes in the manufacture of pesticides involves strict process controls, to reduce to a minimum the wastes which must be treated, and advanced waste treatment measure, to successfully treat toxic wastes prior to their release to the air or water.

Many methods are used to recover plant wastes. Curbs and collecting sumps are placed around pumping areas. Tanks are used to collect pump drippings and accidental losses. Such lost material may be returned to the process. Drain tiles, connected to a collecting sump, catch contaminants which may have seeped into the ground. Filters and scrubbers recover particulates. Industrial vacuum cleaners are used to immediately clean up spills of dry materials.

Frequently, a buffer unit is placed between the processing plant and the final waste treatment unit. It is a method of control, equalization, and stabilization. If the maximum capacity of the intermediate buffer unit is reached, the waste generating plant is shut down. The buffer unit serves also as a trap so that high process losses can be given additional or different treatment. Buffer units used may be tanks, receiving ponds, or sumps.

Empty containers are never abandoned nor allowed to accumulate in an area accessible to humans or animals. They are either burned, if combustible, or decontaminated, if non-combustible. If not contaminated, rinse solutions are burned in an isolated area away from water supplies.

The treatment of organic phosphorous wastes can vary from lagooning to incineration. The system used by a manufacturer of several varieties of organic phosphorous pesticides was developed to treat a waste stream containing unreacted raw materials, partially reacted materials, cleaning products, solvents and other plant wastes. The steps involved include:

- PH adjustment with lime to form calcium phosphate
- Primary settlings
- Activated sludge processing
- Final settlings
- Sludge thickening
- Sludge dewatering.

The deceleration times may extend to seven to ten days to ensure the destruction of the toxic compounds by the aerobic digestion system.

The off-gases from the production of sigma phosphorus compounds (which include hydrogen sulfide and mercapetents) are incinerated. Residual sludges may be landfilled, sea dumped, or incinerated. In some cases, they are diluted and control fed to streams.

Chlorinated organic compounds produce pollutant solids (dust concentrates and powders), liquids (waste solutions), or gases (vapors and mists). Open burning is not used since the hydrogen chloride (HCl) gas released would cause atmospheric pollution. The HCl volatilized inorganics or other acid gases formed are removed by scrubbing towers and/or activated carbon towers. Solid waste materials are either buried in an area designated for disposal of toxic materials, placed in a permanent stock pile, or sent to a settling pond. Liquid disposal may involve the concentration and incineration of combined wastes.

Other pesticides and their disposal methods include:

- Carbonates are somewhat easier to decompose. They are lower in toxicity, decompose quickly in soil, are insoluble in water, breakdown rapidly in alkali, and burn readily. Mixing with alkali decomposes carbonates. Reaction products may be sent to a sewage treatment facility. Caustic treatment in a settling tank is sufficient for water soluble wastes. Solid wastes, which cannot be easily treated, are buried using landfill techniques. Empty containers are burned in unpopulated areas or else are buried.

- Phenoxy Acids, Salts, and Esters - disposal methods include incineration, ehcmical treatment (chlorination or precipitation), or biological treatment (trickling filters, activated sludge, or sewage lagoons). Deep well disposal is also used.
- Inorganics - three disposal methods are used: (a) burial, (b) incineration, or (c) municipal sewage system.

Generally speaking, there are five methods of ground disposal used.

- Deep-Well - dug far from fresh water sources. Noxious fluid wastes are disposed of.
- Sanitary Landfill - refuse is reduced to smallest possible volume, then covered with earth after each day's operation. There exists here the possibility of ground and surface water pollution.

- Disposal Pits - excavations or dumps for the disposal of waste materials. They are left open to the air for extended periods of time. In addition, disposal of waste, both solid and liquid, is not controlled. Waste is dumped haphazardly, is not compacted and covered, and is left exposed to the elements.
- Lagoons - shallow excavations or natural topographic depressions used as retention basins or ponds. The waste is oxidized or degraded biologically, suspended solids settling to the bottom, and evaporation then reduces the amount of effluent to be disposed of. However, there exists the great potential of ground and surface water pollution because the wastes are already in a fluid state.
- Surface - liquid and solid wastes are evenly distributed on selected soil surfaces for pesticide degradation by oxidation, microbial metabolism, or photochemical transformation. If the pesticides are not rapidly metabolized, the possibility for reappearance of the unaltered pesticide in the environment is high.

Although pesticides are designed for widespread use on land, careful control of plant effluents is essential to the health of nearby streams. Unless care is taken to decompose these compounds by chemical, biological or thermal means, the persistency of some pesticides may permit them to leach into the underground water system.

Pesticides which enter streams may also enter the ecological chain by being taken up by plankton and subsequently eaten by higher levels of aquatic life until concentrated into edible fish species. Regulatory agencies and public interest will serve to advance the management and handling systems for these compounds.

SIC 2892 - EXPLOSIVES

1. COMMERCIAL EXPLOSIVES INDUSTRY

The commercial explosives industry comprises all establishments engaged in production of sporting powder, blasting powders, high explosives, nitrated carbohydrates, safety fuses, and detonating caps, but excluding government-owned/contractor-operated (GOCO) munitions plants, small arms ammunition manufacturers and pyrotechnic plants. The SIC code for this category is 2892. Much of the Census data is based on combination of GOCO plants with the commercial industrial installations; adjustments have been made in the Census data to suit the requirements of this part of the report.

The industry includes some 85 establishments, which in 1967 shipped approximately $230 million worth of primary products as opposed to approximately $17 million worth of secondary products for a 93 percent specialization rate (relative value of primary shipments to total shipments). Some 80 of the 85 establishments had specialization rates of 75 percent or greater. There was a total of 10,200 employees in 1967 in the commercial plants; 9,600 worked in plants producing primarily explosives, and of these, 9,000 worked in plants with specialization rates over 75 percent. Thirty-one plants had fewer than five employes, 29 more had fewer than 100 employees, and 20 more had fewer than 500 employees.

The product mixture of the commercial explosives industry in 1967 included:

Blasting Caps - 168.7 million units	$35,800,000
Safety fuse and other blasting accessories	28,400,000
Permissible high explosives, 237.5 million lbs. (approved for underground mining)	42,000,000
ANFO explosives, 434.4 million lbs.	26,400,000
Slurried and high explosives, 337.9 million lbs.	51,900,000
Industrial explosives, black and smokeless powders, propellants	29,800,000

In the period 1963-1967, the total volume of all high explosives increased by about 20 percent. The volume of blasting caps increased by roughly 5 percent in this period, but the value shipped increased about 29 percent. The overall value of shipments for the industry as a whole increased by about one-third over this period.

The industry consumed in 1967 roughly 226,000 short tons of anhydrous ammonia, 107,000 short tons of ammonium nitrate, and 370,000 short tons of sulfuric acid purchased from other establishments. It is unclear from the published information whether this includes transfers from one plant within the industry to another, and whether this includes purchases by GOCO plants. Likewise, there are incomplete figures for in-plant manufacture and total consumption for 1967. It can be noted, however, that roughly comparable quantities of materials were produced in-plant as were purchased in the 1963 period, which would indicate that the total consumption of these materials in 1967 could be of the order of 500,000 short tons each. This figure is not unreasonable in the light of the increased tonnages of shipments in 1967, but is only valid as an order of magnitude estimation. The industry also consumes large amounts of various organic materials (unspecified in the Census data) and some $22 million in packaging and supplies of other natures not specified, in the 1967 reporting period.

2. WASTE MATERIALS

The general waste material generation characteristics of the commercial explosives industry is not clearly separable from the chemical industry as a whole with the exception of two specific kinds of waste materials:

- Waste product materials
- Contaminated packaging.

In other respects the waste material generation is identical to that obtained from large commercial chemical establishments producing basic industrial chemicals such as ammonia, nitric acid, sulfuric acid, acetic acid and certain common organic chemicals. To avoid repetition of previously specified data, only wastes characteristic of the explosives industry (as opposed to the basic chemicals industry) are discussed. Table A-5-22 shows the distribution of materials, locations, and volumes.

The sole method of waste disposal currently used for these materials is open burning, except for some primer materials detonated under water. The frequency of disposal is generally daily, although some smaller volume wastes are destroyed on a weekly, monthly, or even annual basis.

As indicative of the types of process wastes obtained in commercial explosives manufacture, the following data for smokeless powder and for nitroglycerine was taken from "Industrial Wastes: Their Disposal and Treatment," an ACS Monograph edited by William Rudolfs. These materials were considered most significant as

Table A-5-22
Distribution, Locations and Volumes of Explosive Manufacturing Wastes

Federal Region	2	2	3	4	5	5		7	8	8	10
Quantities in pounds per day Location Waste Material	(S. E.) New York	New Jersey	E. Pennsylvania	W. Virginia	N. Alabama	S. Illinois	Ohio	S. Missouri	Utah	Colorado	Washington
Nitroglycerine & NG Mixtures	-	-	-	800	125	10	15	200	10	-	525
Cont. Waste Packaging	-	-	-	800	200	-	-	150	-	-	750
Combined Total	-	-	830	1600	325	10	15	1000	10	-	1275
Smokeless Powder	-	1000	-	-	-	-	-	-	-	-	-
Cont. Packaging	-	3	-	-	-	-	-	-	-	-	-
Combined Total	-	2003	-	-	-	-	-	-	-	-	-
Industrial Exp. & Prop.	-	20	125	-	-	100	-	-	50	-	-
Cont. Packaging	-	-	750	-	-	1000	-	-	250	-	-
Combined Total	-	20	1705	-	-	1100	-	48	300	-	-
Primer Materials & Caps	1	220	-	-	5	-	X	-	-	-	-
Cont. Packaging	1	650	-	-	2	-	-	-	-	-	-
Combined Total	2	870	415	-	7	-	X	-	-	5	-
Regional Total	2	3000	2950	1600	330	1110	15+	1050	310	5	1275

X - Materials detonated; quantity unspecified.

Notes: (1) Combined totals exceed sums of specified parts due to variance in reports from firms.

(2) This table represents reports from four major firms, only, and is not a complete inventory of rates of generation or locations; 6000 other plant operations are treated in a subsequent section.

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*Institute of Makers of Explosives, 420 Lexington Avenue, New York.

representing opposite extremes in explosives manufacturing processes as regards waste proportion to product, and as representing the principal types of explosives manufactured commercially. (ANFO and slurried blasting agents are not processed compounds as such, but are mixtures of common industrial chemicals, generally field mixed or prepared in local mixing plants.)

Pounds Waste per 100,000 lbs. of Explosive

Waste Material	Smokeless Powder	Nitroglycerine
Sulfuric Acid	100,000	5,100
Sulfates	59,800	1,800
Nitrates (N)	108	211
Nitrates (N)	25,500	5,740
BOD	2,460	197
Alkalinity ($CaCO_3$)	-	4,740
Hardness ($CaCO_3$)	15,500	1,440

Acid process residue can be reconcentrated and reused. Acid wash waters are generally neutralized with an alkaline material such as dolomitic lime. Solvents are generally recovered for reuse.

3. MILITARY EXPLOSIVES INDUSTRY

Military explosives manufacturing is conducted principally by the U. S. Army Munitions Command through the Army Procurement and Supply Agency, which has overall production supervision responsibility over 26 Government-owned/contractor-operated (GOCO) plants located principally east of the Rocky Mountains (see Figure A-5-10). Production capabilities under full mobilization would make this operation the eighth largest industry in the nation. Under normal circumstances, the quantities of material produced, while greatly less than full mobilization capability, are still of the order of hundreds of tons daily for each of the different product lines.

Engineering supervisory control over the GOCO plants is divided into two basic areas, according to the type of materials or operations involved. Groups at Picatinny Arsenal, Dover, New Jersey, hold responsibility for explosives manufacturing and load-and-fill operations, whereas fabrication of metal parts and manufacture of small arms ammunition is the responsibility of corresponding groups at Frankford Arsenal, Philadelphia, Pennsylvania.

The principal categories of waste materials generated in munitions manufacture are:

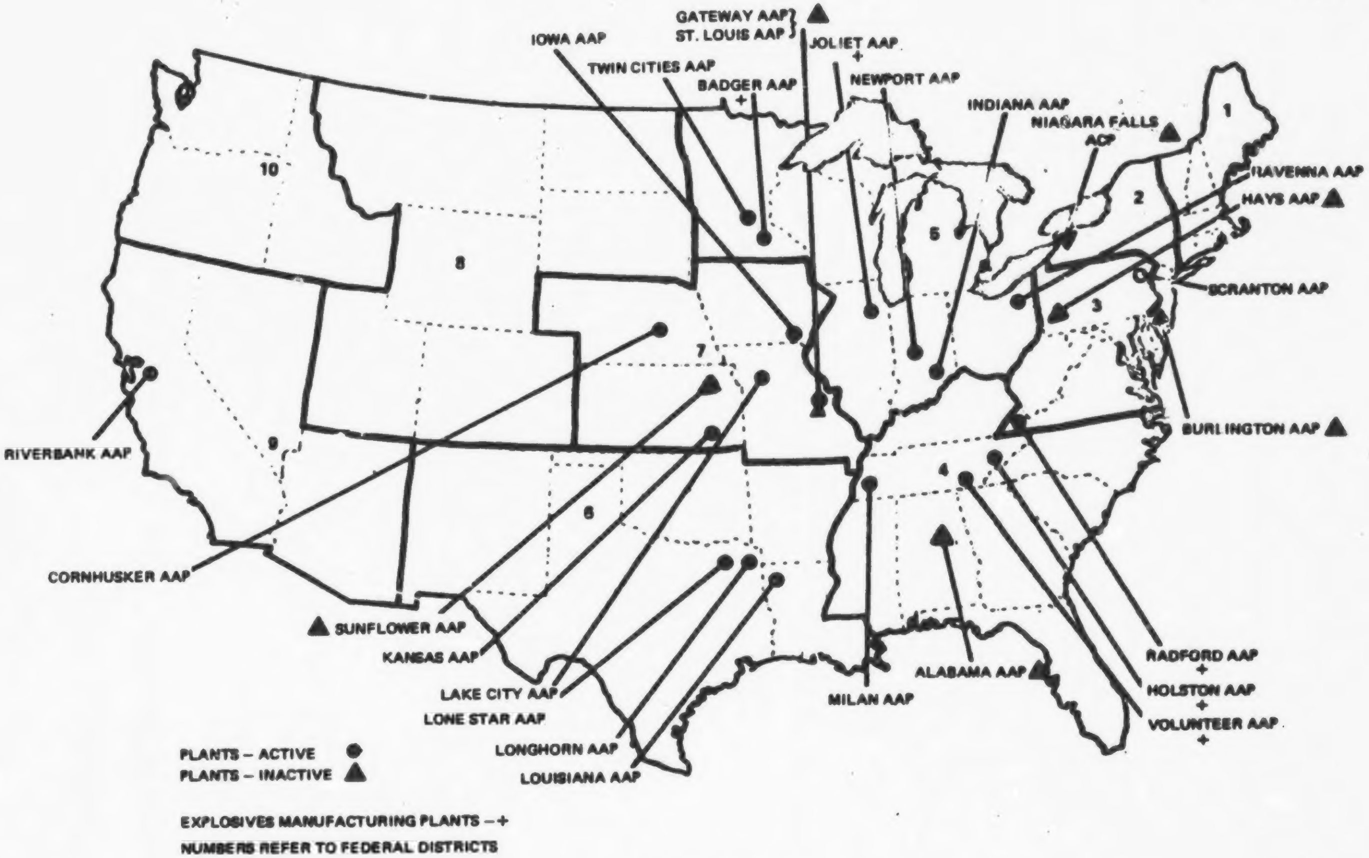

GATEWAY AAP
ST. LOUIS AAP
IOWA AAP
TWIN CITIES AAP
BADGER AAP +
JOLIET AAP +
NEWPORT AAP
INDIANA AAP
NIAGARA FALLS AOP
1
2
3
4
5
6
7
8
9
10
RAVENNA AAP
HAYS AAP
SCRANTON AAP
BURLINGTON AAP
RIVERBANK AAP
CORNHUSKER AAP
SUNFLOWER AAP
KANSAS AAP
LAKE CITY AAP
LONE STAR AAP
LONGHORN AAP
LOUISIANA AAP
MILAN AAP
ALABAMA AAP
RADFORD AAP +
HOLSTON AAP +
VOLUNTEER AAP +
PLANTS – ACTIVE ●
PLANTS – INACTIVE ▲
EXPLOSIVES MANUFACTURING PLANTS – +
NUMBERS REFER TO FEDERAL DISTRICTS

FIGURE A-5-10
U.S. Army Munitions Command
Installations and Activities

- Metal finishing wastes
- Explosives manufacturing process wastes
- Off-spec product; contaminated packaging

Metal treatment wastes include free and emulsified oils, acids (sulfuric, phosphoric, chromic, and hydrochloric), soaps, alkaline washes, cyanides, nitrates, chlorides, and barrium, lead, chromium, iron, copper and tin salts. Difficulties in treatment center more on continuous process modifications, nonseparability of waste streams, unavailability of monitoring techniques, and indefinite information on materials discharged rather than on lack of available abatement technology.

Explosives manufacturing processes produce the most serious problem in pollution abatement both quantitatively and technologically. Explosives manufacturing involves production of large quantities of heavy acids (sulfuric, nitric, acetic), nitration of organic compounds, and product refinement, washing and drying. The types of waste generated include: nitrates, acetates, suspended explosive solids, sulfates, some sludges, red water, and organic explosives and solvents. Acetates are associated with production of RDX and HMX, red waters with TNT and DNT. The other materials are common to all explosives manufacturing processes. Both manufacturing plants and loading plants face the problem of disposing of unwanted explosives and contaminated packaging. Loading plants also have difficulties with red waters and with residues from primer compounds (lead azide, lead styphnate and arsenic compounds).

Efforts have been initiated within the cognizant agencies to correct the problems of water, air, and land pollution associated with these operations. Studies have been conducted on the economics of the various possible approaches, and the decision was made to initiate an overall modernization program in combination with a pollution abatement program to ultimately eliminate all harmful effluents, however borne. (Most of the GOCO plants were engineered and constructed during World War II. Requirements of an intermittent nature since have resulted in modifications to lines to the extent that some plants now are geared for 200 percent of design capacity. Design evaluation studies show that modernization can in most cases be the most effective and economical means of reducing waste problems.)

Gradually the more active plants (Holston, Radford, Volunteer, Joliet) have been developing process waste stream treatment schemes which rely principally on recycling and reclamation steps to reduce costs and reduce wastes. Incineration techniques for explosive wastes and contaminated packaging are at various stages of development, but the primary problem is that of preparation of the waste for incineration, not that of incineration efficiency. The most common form for disposal of sensitive wastes is detonation or open burning; contaminated packaging is usually open-burned also. The danger of accidental detonation in incinerators or pre-treatment units is currently considered too great to allow use of such methods of disposal without extensive development.

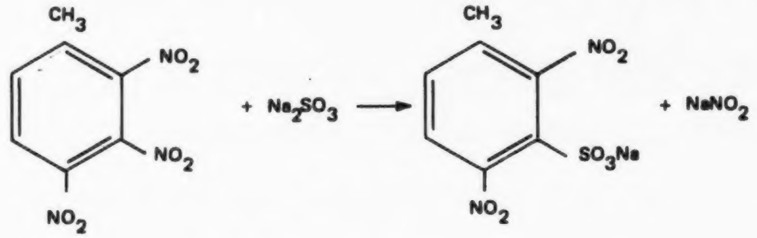
The contractors operating GOCO plants are responsible for all waste disposal according to terms of the operating agreements. The supervising agencies, as part of the U.S. Army Munitions Command's overall modernization and pollution abatement program, are preparing survey reports detailing the waste treatment problems at all such plants, however. The survey program is currently expected to be complete by July 1972. At this time, Holston Army Ammunition Plant and Radford Army Ammunition Plant are most advanced with respect to the survey. The objectives of the study are fourfold: (1) identify pollutants (air, water, land); (2) identify sources; (3) specify current practice and evaluate; and (4) specify proposed abatement program.

Specific information on various manufacturing processes and certain plant operating characteristics are presented below to provide a basis for understanding the magnitude, nature, and proposed countermeasures. Where possible, charts and diagrams have been reproduced from original material to achieve the data transfer in as efficient a manner as possible.

4. SPECIFIC PROCESSES AND PLANTS

(1) TNT Manufacture

Manufacturing of TNT via nitration of toluene by a mixture of sulfuric and nitric acids results in two principal waste materials. The first is the spent acid stream, which can be reclaimed. The second waste is the "red water" from the purification process. The trinitration reactions yield some 95.5 percent b. w. of the desired 2, 4, 6 isomer; the remaining 4.5 percent b. w. is removed by treatment with sodium sulfite, giving a structure of the form shown below:



The characteristic "red water" stream from the selliting process has the following composition:

Water	77.6%	Sodium Sulfite	2.3%
Organics	17.3%	Sodium Nitrate	1.7%
Sodium Nitrite	3.5%	Sodium Sulfate	0.6%

(Due to conflicting analytical methods, total exceeds 100%.)

There is currently only one disposal technique employed for red water waste: concentration followed by incineration, producing

NOx and SOx emissions and solid sodium sulfate. After concentration, some of the red water is sold to the paper-manufacturing industry as a source of sulfite liquor, but this avoidance of incineration is practical at only certain plants located near paper-producing areas of the country. The sodium sulfate produced by incineration is currently merely accumulated. The approximate quantitative relationships in the overall process are:

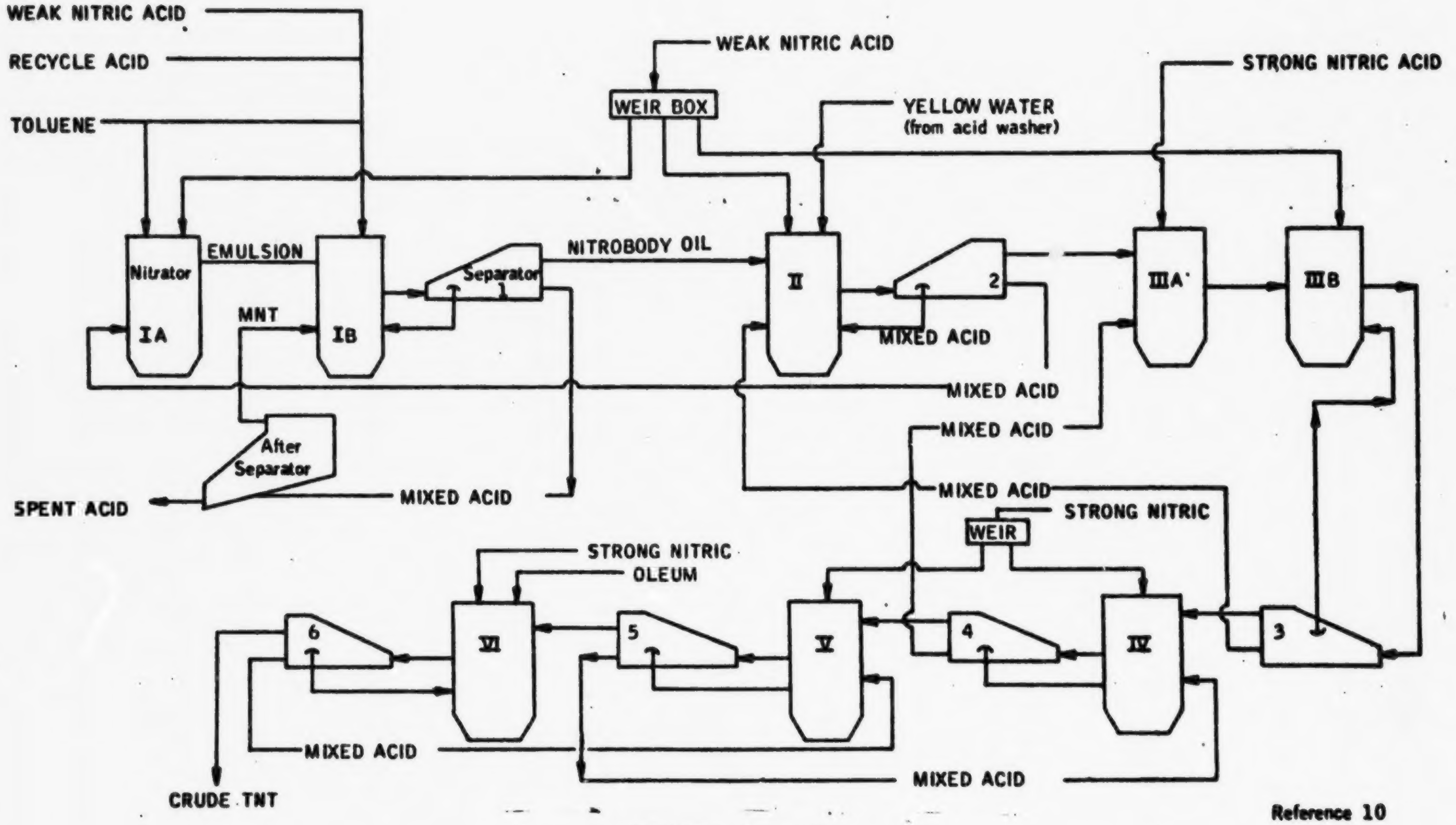
100 lbs. TNT produced gives: 34 lbs. "red water" containing
26.5 lbs. water
5.9 lbs. organics (nitrotoluene sulfonic acids)
1.6 lbs. dissolved inorganic salts

which on incineration yields approximately 2.5 lbs. sodium sulfate. Although production figures are not readily available, TNT production currently results in generation of over 1,000 tons of sodium sulfate annually, by estimate based on very incomplete data (see Figure A-5-11).

Two principal alternatives to incineration have been proposed:

- Regeneration of DNT, renitration to TNT (acidification)
- Regeneration of sodium sulfite (fluid bed or Tampella process).

Acidification recycles the DNT in the waste and eliminates wastes altogether. Four other exploratory programs are contemplated


WEAK NITRIC ACID
RECYCLE ACID
TOLUENE
WEAK NITRIC ACID
WEIR BOX
YELLOW WATER (from acid washer)
STRONG NITRIC ACID
Nitrator
IA
EMULSION
MNT
IB
Separator 1
NITROBODY OIL
II
2
MIXED ACID
IIIA
IIIB
MIXED ACID
MIXED ACID
After Separator
SPENT ACID
MIXED ACID
MIXED ACID
WEIR
STRONG NITRIC
STRONG NITRIC
OLEUM
6
VI
5
V
4
IV
3
MIXED ACID
MIXED ACID
CRUDE TNT

Reference 10

FIGURE A-5-11
Flow Diagram for Continuous Process
TNT Manufacture*

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*From Goldstein, Raymond. Trip Report to Radford Army Ammunition Plant, 24 October 1968. Picatinny Arsenal. UNCLASSIFIED Report.

which are directed towards changing the manufacturing process, but these are largely untried as yet.

There are two other wastes characteristics of TNT manufacture which are quantitatively smaller but still serious. The first is suspended TNT in waste acid streams and wash waters. (This waste is also encountered in all loading and formulation plants using TNT.) Effluent containing more than 5 ppm TNT is considered deleterious to the environment, and two possible solutions are being considered:

- Liquid/liquid extraction with toluene, TNT recovery
- Adsorption of TNT on activated carbon, and subsequently
    - Toluene wash to regenerate carbon, recover TNT
    - Thermal regeneration of carbon, destruction of TNT

Thermal regeneration of carbon would require control of NOx/SOx emissions.

The second of these quantitatively lesser problems is the disposal of tetranitromethane (TNM) produced as a gaseous by-product of the trinitration process. TNM is a very dangerous explosive, alone or with other organic materials, and its vapors are currently discharged to the air rather than being collected. A relatively unstable material and sensitive to sunlight, TNM has not been observed to accumulate on discharge. Some TNM is found in acid and fume recovery systems, however, and pilot studies are in progress to determine the feasibility of decomposing all TNM produced catalytically to reduce emissions and simultaneously improve process safety.

(2) RDX/HMX Manufacture

The nitration of hexamine to RDX and HMX occurs by the action of nitric acid, ammonium nitrate, acetic acid and acetic anhydride. A process flow sheet based on 100 pounds of reactor charge is shown on the following page. Although production figures are again not readily available, an appreciation of the volume can be obtained by the fact that catch basin figures are based on 100 tons of explosive per day per building, and at least one line is normally in operation. The nitration process per se produces a slurry of explosive in acid; the only wastes are materials recovered from the acid vapor scrubber stream. Some NOx, some acetic acid, formic acid and some methylnitrate escapes from the scrubber.

The next series of processes involves recovery of virtually all of the by-products of the reaction simultaneously with purification of the RDX and HMX products. With the exception of losses through the recovery systems, no wastes are allowed to be generated. Essentially all of the by-products are recycled to starting material production plants. The particular plant from which this data is taken is Holston Army Ammunition Plant, (see Figures A-5-12, 13, and 14) where acetic anhydride and nitric acid are manufactured for use in RDX/HMX production, and the RDX produced is incorporated with TNT produced elsewhere to form Composition B. (The wastes from the acid and anhydride manufacturing processes are not discussed here, as they are characteristic of chemical manufacturing rather than munitions manufacturing.) Thus, the nitrobodies accumulated in the plant catch basins include both RDX/HMX (from manufacturing and incorporation lines) and TNT (from incorporation lines). The current practice for disposal of materials recovered from catch basins is open burning; any RDX/HMX found to be contaminated with glass is also open-burned, as it is too easily initiated when so contaminated. On a quantitative basis, production of 100 tons of RDX yields approximately 160 pounds of acetic acid and one pound of explosive in the catch basin effluent (BOD 878 COD 112) as opposed to influent of 160 pounds acetic acid and two pounds of explosive (BOD 979 COD 1177). The balance of catch basin sludge is a mixture of organic and inorganic salts; essentially

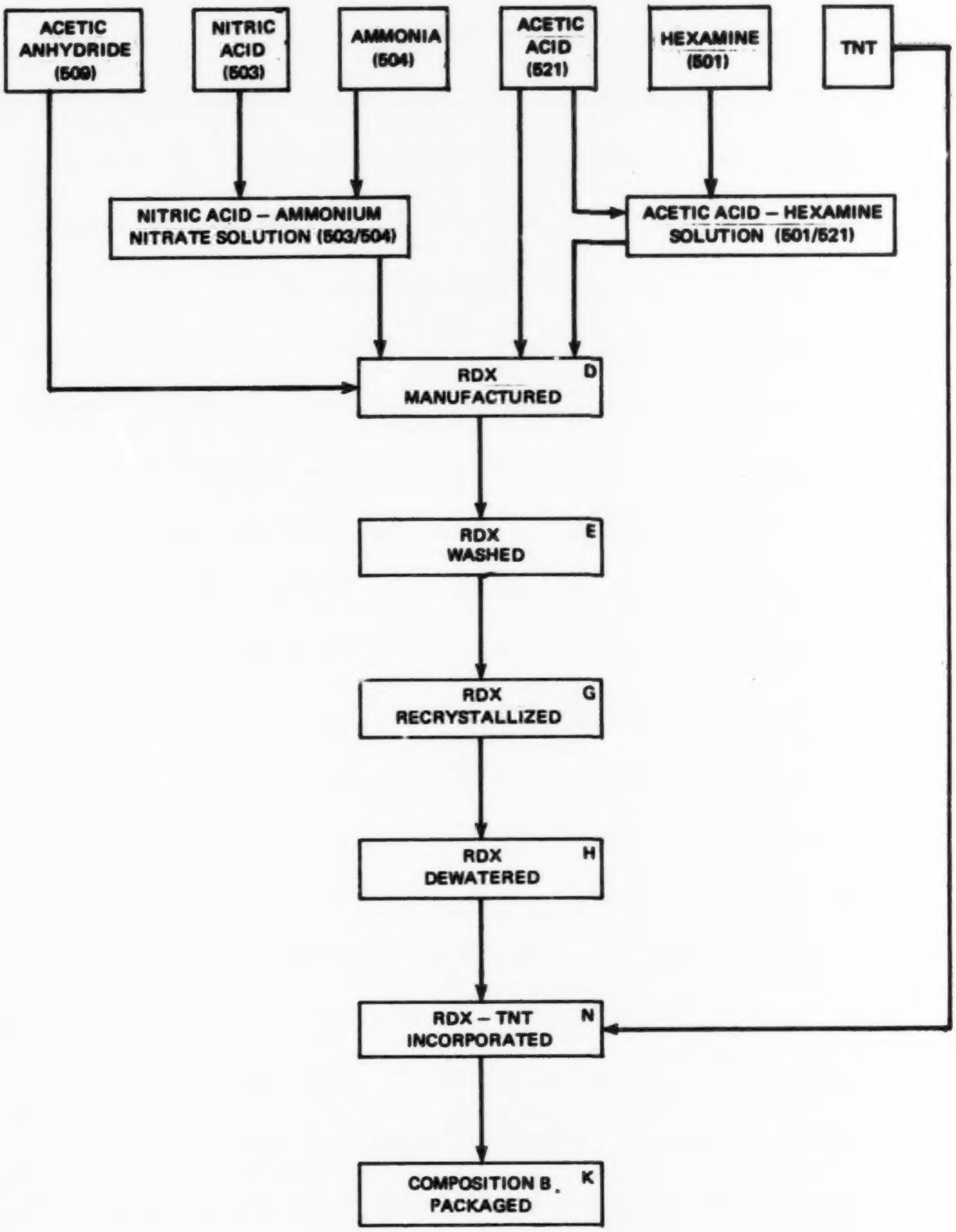
ACETIC ANHYDRIDE (509)
NITRIC ACID (503)
AMMONIA (504)
ACETIC ACID (521)
HEXAMINE (501)
TNT
NITRIC ACID – AMMONIUM NITRATE SOLUTION (503/504)
ACETIC ACID – HEXAMINE SOLUTION (501/521)
RDX MANUFACTURED D
RDX WASHED E
RDX RECRYSTALLIZED G
RDX DEWATERED H
RDX – TNT INCORPORATED N
COMPOSITION B PACKAGED K

FIGURE A-5-12
Process Flow at HAAP

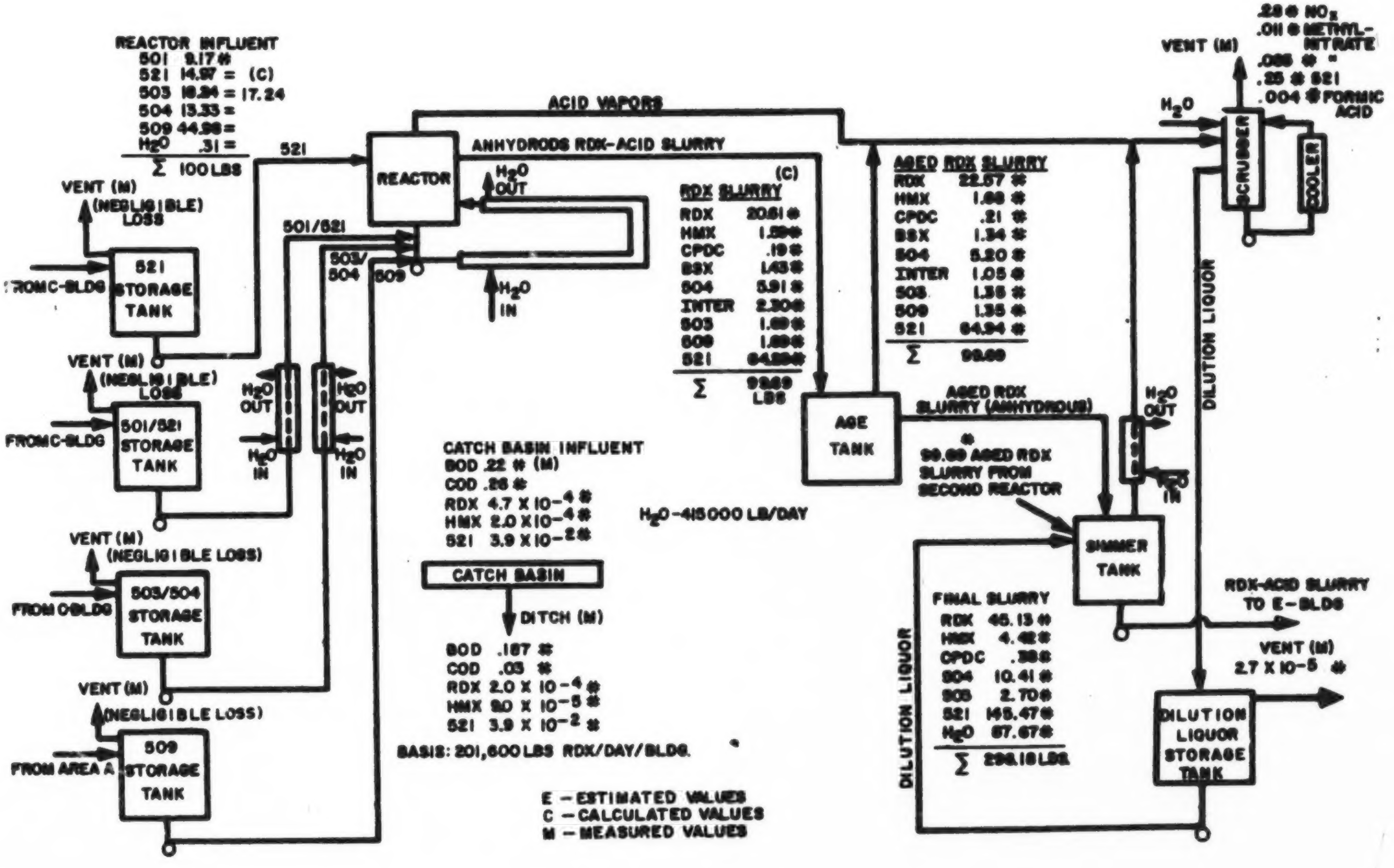
REACTOR INFLUENT
501 9.17#
521 14.97 = (C)
503 16.24 = 17.24
504 13.33 =
509 44.98 =
H2O .31 =
Σ 100 LBS
VENT (M)
(NEGLIGIBLE) LOSS
521 STORAGE TANK
FROM C-BLDG
VENT (M)
(NEGLIGIBLE) LOSS
501/521 STORAGE TANK
FROM C-BLDG
VENT (M)
(NEGLIGIBLE LOSS)
503/504 STORAGE TANK
FROM D BLDG
VENT (M)
(NEGLIGIBLE LOSS)
509 STORAGE TANK
FROM AREA A
521
501/521
503/504
509
H2O OUT
H2O IN
H2O OUT
H2O IN
REACTOR
H2O OUT
H2O IN
ACID VAPORS
ANHYDRODS RDX-ACID SLURRY
(C)
RDX SLURRY
RDX 20.61#
HMX 1.59#
CPDC .19#
BSX 1.43#
504 5.91#
INTER 2.30#
503 1.69#
509 1.69#
521 64.29#
Σ 99.69 LBS
CATCH BASIN INFLUENT
BOD .22 # (M)
COD .26 #
RDX 4.7 X 10-4 #
HMX 2.0 X 10-4 #
521 3.9 X 10-2 #
CATCH BASIN
DITCH (M)
BOD .187 #
COD .03 #
RDX 2.0 X 10-4 #
HMX 9.0 X 10-5 #
521 3.9 X 10-2 #
BASIS: 201,600 LBS RDX/DAY/BLDG.
H2O-415000 LB/DAY
E - ESTIMATED VALUES
C - CALCULATED VALUES
M - MEASURED VALUES
AGE TANK
AGED RDX SLURRY
RDX 22.57 #
HMX 1.68 #
CPDC .21 #
BSX 1.34 #
504 5.20 #
INTER 1.05 #
503 1.35 #
509 1.35 #
521 64.34 #
Σ 99.69
AGED RDX SLURRY (ANHYDROUS)
# 99.69 AGED RDX SLURRY FROM SECOND REACTOR
H2O OUT
H2O IN
SIMMER TANK
FINAL SLURRY
RDX 45.13 #
HMX 4.42 #
CPDC .38 #
504 10.41 #
503 2.70 #
521 145.47 #
H2O 87.67 #
Σ 298.18 LBS
DILUTION LIQUOR
DILUTION LIQUOR
RDX-ACID SLURRY TO E-BLDG
VENT (M)
2.7 X 10-5 #
DILUTION LIQUOR STORAGE TANK
VENT (M)
H2O
.29 # NOx
.011 # METHYL-NITRATE
.085 # "
.25 # 521
.004 # FORMIC ACID
SCRUBBER
COOLER

FIGURE A-5-13
D-Building, Manufacture of RDX

Scrubber Vent

3500 PPD N_2O	
49 PPD	**Methyl Acetate**
153 PPD	**Methyl Nitrate**
533 PPD	**Acetic Acid**
17 PPD	**Formic Acid**

Main Effluent	**BOD**	**COD**	**RDX**	**521**
Catch Basin Influent	979	1177	2.1	160
Catch Basin Fffluent	878	112	.96	160

Storage Tank Vents

Negligible

FIGURE A-5-14
D-Building Pollutants
Basis 201,600 PPD RDX Mfg.

all of the catch basin influent comes from equipment cleansing operations. Design of new explosive waste incinerators for these materials is now proceeding in conjunction with other efforts towards biodegradation of nitrobodies.

One waste associated with RDX/HMX manufacture, metylnitrate is both toxic and explosive. Although the quantities generated are of the order of 200 pounds per 100 tons of RDX produced, the problem is considered sufficiently serious that a program of recovery from the gaseous effluents, combination with amounts recovered from acetic acid purification, and catalytic decomposition or hydrogenation to destroy the nitrate is scheduled for FY 1973. Design of new explosive waste incinerators for these materials is underway in conjunction with other efforts toward biodegradation of nitrobodies.

(3) Propellant Manufacture

Propellant manufacturing includes a number of processes involving production of nitroglycerine, nitrocellulose and nitroguanidine. The principal wastes in these processes are nitrobodies of a non-aromatic nature, some of which have been escaping as losses in wash waters (9000 lbs. /day nitrocellulose fines are lost at Radford). The magnitude of the problem is expected to be greatly lessened by currently planned water purification improvements. The nitrobodies will be reclaimed where possible; where recovery is unsatisfactory, the material will be treated by biodegradation or incinerated.

Current treatment of nearly all explosive wastes not suitable for reclamation is open-burning. Contaminated nitrogylcerine is frequently purposely detonated, however, due to its extreme sensitivity, unpredictability and power, it is virtually never put through a recovery process.

(4) Primer Materials

Lead styphnatel primer manufacture is of the order of 15 tons per month, 35 percent of which is lead styphnate and 77 percent of which is tetrazine. The balance of the primer mix is PETN (pentaerytritol tetranitrate), aluminum and inorganic salts. The waste by-products include lead and sodium nitrates and acetates, styphnic acid (trinitroresorcinol), nitrated sulfonic acids of resorcinal, aminoguanidine acetate and sodium nitrite. The principal current method of treatment is open burning for explosive materials. Planned process modifications are expected to relieve some problems (changing explosive wastes to non-explosive wastes), but waste disposal planning is still in its early stages.

(5) White Phosphorous Waste

White phosphorous wastes are a product of shell loading plants, where the material is carried away primarily in cleaning and excess removal operations. Treatment is currently undeveloped. Current planning is for oxidation to phosphoric oxide and conversion to usable orthophosphoric acid. No quantitative data is available at this time.

(6) Contaminated Packaging Disposal

As mentioned previously, current practice for disposal of all contaminated packaging is open-burning. A program of incinerator development for disposal of such materials has been initiated, however. Joliet and Cornhusker plants are proceeding with semi-independent efforts towards equipment of different capacities. The approximate volumes of contaminated waste packaging at four major plants are:

Plant	Contaminated Waste	Non-contaminated Waste
Cornhusker	400,000 lbs/month	60,000 lbs/month
Joliet	60,000	540,000
Radford	160,000	54,000
Volunteer	10,400	0

5. ORDNANCE DISPOSAL

The disposal of unservicable ordnance is a problem common to all branches of the armed services. As a matter of historical development, however, the largest quantities of large-scale ordnance have been dealt with by the Navy, on behalf of all three services. Earlier forms of ordnance were relatively easy to desensitize, disassemble and dispose of. In the more recent past, efforts to prevent use of captured ordnance by enemy forces have resulted in design of "tamper-proof" munitions. Unfortunately, this design makes disposal of unserviceable ordnance by "demilitarization" both difficult and dangerous, and the armed forces established the practice of dumping at sea as the safest and most effective method of disposal. Efforts to resolve the safety problem in other forms of disposal have continued, but the amount of material to be dealt with is enormous and the results of accidents are extremely serious. No deep water dumping is now permitted, and current demilitarization facilities are not capable of disposing of the quantities of material involved, so the ordnance is currently being accumulated.

(1) Quantities

To exemplify the magnitude of the problem, current estimates of the backlog of ordnance requiring disposal range between

80,000 and 120,000 tons, including:

Explosive Projectiles
Small Arms Ammunition
Fuses
Detonators
Primers
Grenades
Solid Propellants
Firing Devices
Pyrotechnics
Ejection Cartridges
Rockets
Bombs
Depth Charges
Rocket Motors.

These items range from small handgun cartridges to 16" shells. Individual items weigh up to several tons in some cases. Numerically, as examples, some 100,000,000 rounds of ammunition below 20mm are included; no numerical estimates of the number of other items have been located.

(2) Demilitarization

Time-consuming expensive and dangerous demilitarization operations could, it is estimated, result in disposal of roughly 50,000 tons of the total backlog, allowing reclamation of 7,000 tons of HBX, 6,000 tons of TNT and 15,000 tons of smokeless powder. The procedure varies as a function of the specific type of ordnance being treated. Small rounds (up to 20mm) are separated (projectile form cartridge case), the powder is burned and the projectile and cartridge case "popped" in a retort furnace ("popping" = detonation of primers by heat). The metal is recovered for scrap, and it is possible to design the system to recover and reprocess the powder. Larger units are first defused; the explosive charges are removed by washing, steaming or drilling. The explosive is then either recovered or burned, and the metal is recovered for scrap.

The hazards of the demilitarization operations are significant. A single MK-51 underwater mine contains 3,200 pounds of TNT, for example. Successful demilitarization of these mines has resulted in reclamation of over 2,400 tons of TNT in the immediate past. The problems of successful demilitarization are apparent to those who have experience with use of ordnance devices and explosives and are compounded by the fact that large quantities of high explosive devices are handled simultaneously. Many explosives which are easily burned in the open without detonation are extremely subject to detonation when encased in metal sheaths. At least one incident has occurred in the fairly recent past in a 20mm demilitarization line where a sudden accumulation of some 20,000 rounds detonated in a retort furnace. The details of the incident are not clear, but the entire processing unit was completely destroyed, leaving a sizable crater.

(3) Destructive Disposal

Two other methods of disposal are currently in use which involve intentional discharge or detonation of ordnance. Smaller items are simply dropped into contained fires through tubes, in the fire they explode and the metal is recovered for scrap. A second program involves burial of large amounts of ordnance in pits; these charges are primed and tamped with 10 to 16 feet of earth and detonated. Roughly 40 pits are detonated daily, disposing of some 40 tons per day. The entire series is detonated over a 200-second interval. As of September 1971 one such group was in operation on a five-day week basis. At this rate, this group would require eight to twelve years to work off the current inventory; alternatively, ten groups might dispose of the inventory in one year. Thereafter, however, as much as 20,000 tons of material would be handled annually, requiring two groups full time to merely detonate the normal accumulation. In addition to the problems of manpower, and cost and environmental unpleasantness at the least, the long duration safety and land use problems are unclear.

At least one incinerator for destruction of some 500 tons of miscellaneous fuses is under construction at the Earle Naval

Facility. This unit is designed to meet both safety and pollution regulations, but is as yet a prototype design. The performance of this unit from both points of view is still undefined.

(4) Deep-Water Dumping

The practice of deep-water dumping, as mentioned above, has been discontinued. This method of disposal accounted for some 100,000 tons of unserviceable ordnance over the period 1964-1971 in the Maritime Administration Hulk Numbered Deep Water Dumps system alone. According to this system, an obsolete vessel (merchantman) was stripped free of all but fixed elements of the structure and the fuel tanks cleaned thoroughly. The ordnance was then stowed to give maximum density (more buoyant items packed in 55-gallon drums filled with concrete), the hulk was towed at least ten miles from shore and scuttled in at least 500 fathoms depth. The dumping areas were selected to reduce the probability of fish kills in the event of detonations, which were sometimes intentional. Such intentional detonations were performed at the request of the international scientific community, occasionally unplanned. In most cases, the hulk bottomed without detonations, and in no case did detonation occur prior to scuttling. A dump of this type might range up to 8,500 tons at a time, but was generally in the broad vicinity of 5,000 tons.

Small-scale deep water dumping practices were commonly conducted for many years as ordnance disposal methods. Such operations involve jettisoning up to 250 tons of material at a time in sites meeting the ten-mile, 500 fathoms criteria mentioned above. The actual dumping is performed over a short period of time, rather than all at once. No detonation has ever been experienced in operations of this type. Of 13 sites selected for such dumps in 1971, only one lay less than 20 miles from shore (12,000 feet deep). All liquid propellants, industrial chemicals and chemical agents were excluded from this type of disposal.

(5) Other Proposals

Proposals have been made regarding design of mobile demilitarization lines to reduce the need for overland transportation of munitions. The question of safety is not attacked in this particular solution to part of the problem, but further developments in both demilitarization technology and new forms of ordnance construction are expected to alleviate the danger in the future. Detonation in AEC caverns, in conjunction with AEC tests, and in abandoned mine shafts has been proposed also. This reduces the processing danger somewhat but requires substantially more overland transportation and handling. Biodegradation and more effective forms of chemical treatment are two possible routes to safer demilitarization, but we still are very far from achievement, so far as has been discovered.

6. ROCKET PROPELLANTS

Rocket propellants are broadly divided into two groups: liquid propellants and solid propellants.

(1) Liquid Propellants

Liquid propellants are fundamentally selected industrial chemicals which are further divided into oxidizers and fuels. The bulk of these materials are therefore produced by major chemical manufacturers. The principal liquid fuels are:

Ammonia
Hydrazine*
Monomethyl Hydrazine (MMH)
Unsymmetrical Dimethyl Hydrazine (UDMH)
MHF-3 (MMH and hydrazine)
MHF-5 (MMH, hydrazine, hydrazine nitrate)

Alcohols (prinicpally methanol)
Nitroparaffins (nitropropane)
Hydrocarbons (gasoline, JP4)
Liquid Hydrogen
Aerozine 50 (UDMH and hydrazine)

The principal liquid oxidizers are:

N_2O_4 (nitrogen tetroxide)
RFNA (red fuming nitric acid)
WFNA (white fuming nitric acid)
Liquid Oxygen
Liquide Fluorine
Hydrogen Perioxide*

Chlorine trifluoride
Chlorine Pentafluoride
Bromine Pentafluoride
FLOX (liquid oxygen and liquid fluorine)

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* Also used in catalytic engines as a monopropellant. Detonable in high strengths.

(2) Solid Propellants

The principal solid propellant used in major missiles is aluminized ammonium perchlorate, a mixture of 20 percent finely divided aluminum, 74 percent ammonium perchlorate and 6 percent organic polymer binder. The entire missile motor is produced by one manufacturer who formulates and casts the propellant in the case. Metal parts and component materials of the propellant may be purchased. Generally, the prime motor manufacturer conditions the propellant materials, produces the binder system, formulates the propellant, casts and cures.

The principal waste material from these operations is excess propellant and contaminated component materials. When practical, waste materials are reclaimed. When reclamation is economically unfeasible, the materials are burned in the open. The products of combustion include Al_2O_3, H_2O, CO, CO_2, N_2, chlorides (HCl), NOx, and carbon. A method of reclaiming ammonium perchlorate from outdated grains has been patented (Reference 12) which employs leach water to cool the propellant during shredding operations. The water dissolves the oxidizer, leaving aluminum and shredded binder which can be handled as a "non-hazardous" waste.

Other systems currently in use for smaller missile motors include: double-based propellants (ordinarily nitrocellulose/nitroglycerine/binder systems), ammonium nitrate grains (aluminized and non-aluminzed, similar to preceding discussion), pressed grains (black power, mixtures of inorganic fuels and oxidizers).

The principal constituent materials of solid rocket propellants are:

Aluminum (power or flake)
Ammonium Perchlorate
Ammonium Nitrate
Sodium Nitrate
Potassium Nitrate
Sodium Perchlorate
Potassium Perchlorate
Magnesium Perchlorate
Potassium Permanganate
Sodium Permanganate
Sodium Peroxide
Nitrocellulose
Nitroglycerine
Sulfur (powdered)
Carbon Powder
Binders $(C_2H_4O)_n$

The principal products of combustion are:

Metal Oxides
Water
Nitrogen
Carbon Dioxide
Carbon Monoxide
Hydrogen Chloride
Carbon
NOx
SOx

The principal current method of disposal of solid propellant manufacturing wastes and outdated grains is open burning. At least one patent (Reference 1) has been issued on a recovery process involving elation of oxidizer by cooling water during comminutation of the grain by knives. The oxidizer can be recrystallized and reused, and the inert binder and metal fuel can be further separated for recovery of the metal, either before or after incineration.

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